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RECONDITION AND REUSE OF ORGANICALLY CONTAMINATED WASTE SODIUM CHLORIDE BRINES

Robert D. Fox, et al

Dow Chemical Company

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Recondition and Reuse of Organically Contaminated Waste Sodium Chloride Brines

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10 Author(s)
Fox, R~~obert~~ D.
Keller, R~~ichard~~ T.
Pinamont, C~~arl~~ J.

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27 Abstract

A plant of 100 gal/min capacity was constructed and operated for one year to demonstrate the feasibility to remove and recover phenol and acetic acid from an 18% sodium chloride brine by adsorption on fixed beds of activated carbon. The purified brine was used for production of chlorine and caustic soda. Separate electrolytical test-cell evaluation of the purified brine showed it to be equivalent to pure brine. Regeneration of the carbon was accomplished by desorption with dilute sodium hydroxide. The phenol desorbed was recycled to the phenol manufacturing plant while the acetate regenerant was processed to underground disposal wells. More than 23 million gallons of brine were purified. Fourteen cycles of phenol adsorption and regeneration and 105 cycles of acetic acid adsorption and regeneration were completed with no significant deterioration of carbon performance. Phenol removal to <1 ppm was accomplished at 50-140 gal/min and 15-70°C with an effective carbon capacity of 0.167 lb/lb. Optimum regeneration was with 4% NaOH at 55-70°C. Removal of 90% of the acetic acid from brine requires <80 gal/min flow rate and <40°C temperature, the resultant loading is 0.04 - 0.06 lb/lb of carbon. The projected net cost of purifying this waste brine for reuse was $1.32 per 1000 gallons. The process results are discussed in detail along with costs. (M) (EPA)

Abstractor Carl J. Pinamont	Institution The Dow Chemical Company - Midland, Michigan

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RECONDITION AND REUSE OF ORGANICALLY CONTAMINATED WASTE SODIUM CHLORIDE BRINES

By

R. D. FOX
R. T. KELLER
C. J. PINAMONT

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PROJECT OFFICER
CLIFFORD RISLEY

OFFICE OF RESEARCH AND MONITORING
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ABSTRACT

A plant of 100 gal/min capacity was constructed and operated for one year to demonstrate the feasibility to remove and recover phenol and acetic acid from an 18% sodium chloride brine by adsorption on fixed beds of activated carbon. The purified brine was used for production of chlorine and caustic soda. Separate electrolytical test-cell evaluation of the purified brine showed it to be equivalent to pure brine. Regeneration of the carbon was accomplished by desorption with dilute sodium hydroxide. The phenol desorbed was recycled to the phenol manufacturing plant while the acetate regenerant was processed to underground disposal wells. More than 23 million gallons of brine were purified. Fourteen cycles of phenol adsorption and regeneration and 105 cycles of acetic acid adsorption and regeneration were completed with no significant deterioration of carbon performance. Phenol removal to <1 ppm was accomplished at 50-140 gal/min and 15-70°C with an effective carbon capacity of 0.167 lb/lb. Optimum regeneration was with 4% NaOH at 55-70°C. Removal of 90% of the acetic acid from brine requires <80 gal/min flow rate and <40°C temperature, the resultant loading is 0.04 - 0.06 lb/lb of carbon. The projected net cost of purifying this waste brine for reuse was $1.32 per 1000 gallons.

This report was submitted in fulfillment of Grant No. 12020-EAS between the Office of Research and Monitoring of the U. S. Environmental Protection Agency and The Dow Chemical Company. This project was proposed, designed, and performed by the Environmental Research Laboratory, Dow Chemical U.S.A. at its plant site in Midland, Michigan.

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SECTION I

CONCLUSIONS

1. Waste sodium chloride brine from a phenol manufacturing plant was purified by activated carbon adsorption and recycled to a diaphragm-type electrolytic cell to produce chlorine and caustic soda. The projected net cost of treatment was $1.32/M gal.

2. Purified brine from the activated carbon adsorption process showed no significant difference from pure salt brine when tested in a 2660 amp diaphragm-type electrolytic cell.

3. Separation of organic byproducts from waste brine by adsorption on activated carbon and their recovery by chemical regeneration of the carbon has been demonstrated on an engineering scale in a 100 gal/min Demonstration Plant.

4. Fixed bed activated carbon adsorption columns removed and recovered the phenol from the waste brine down to <1.0 ppm through 14 cycles of adsorption and caustic regeneration.

5. Flow rates of 50-140 gal/min (1.0 to 2.8 gal/min/sq/ft) and temperatures of 15-70°C had no significant effect on the performance of the phenol adsorption system.

6. The effective capacity of the activated carbons tested for phenol adsorption averaged 0.167 lb/lb and no significant deterioration in performance was detected after 14 cycles.

7. In regeneration of the phenol adsorbers, 4% caustic soda solution at temperatures of 50-65°C at a flow rate of 30 gal/min (0.6 gal/min/sq/ft) were better than higher caustic strength and lower temperatures. The peak phenol concentration in the regenerant averaged 6% and the volume of regenerant was 6% of the feed brine treated. The NaOH required for regeneration was 20 lb/M gal brine purified.

8. No difference between Witco 718 and Nuchar WV-G granular activated carbons was observed in phenol adsorption or caustic regeneration.

9. Fixed bed activated carbon columns removed >90% of the acetic acid from the waste brine at temperatures below 40-45°C and flow rates below 80 gal/min (1.6 gal/min/sq/ft). The effective carbon capacity ranged from 0.04 to 0.06 lb/lb.

10. Operation of the acetic acid adsorbers at temperatures greater than 40-45°C resulted in an effective carbon capacity too low to be practical. Poor effluent quality also resulted at these temperatures.

11. Each acetic acid adsorber operated through 105-cycles of adsorption and regeneration. No abnormal decrease in carbon capacity was noted.

12. Witco 718 produced better effluent quality and loading under comparable conditions than did Nuchar WV-G in acetic acid adsorption.

13. Regeneration of the acetic acid adsorbers required 3600-4200 lb of NaOH as 10% NaOH. The peak acetic acid concentration in the regenerant was 55-65 g/l, and the volume of regenerant was 6000 gal, or ~6% of the feed brine treated. The caustic usage was 36 lb NaOH/M gal.

14. The tail portion of the regenerant, being weak in acetic acid, can be saved, fortified with 3600 lb of NaOH and reused as regenerant. The volume of regenerant is thereby reduced to 3500-4000 gal.

15. A method of recovering acetic acid from the regenerant, involving solvent extraction and vacuum distillation, was developed in the laboratory, but the amount and value of acetic acid available for recovery was too low to justify capital expenditure.

16. No correlation of the measured surface properties of the two carbons tested could be made with their performance in the Demonstration Plant.

SECTION II

RECOMMENDATIONS

The activated carbon byproduct recovery and reuse approach to the reduction or elimination of wastes has been demonstrated on an engineering scale and can be recommended for application to the reuse of waste sodium chloride brines to manufacture chlorine and caustic soda. Application to phenol or phenol-type compounds has also been demonstrated using activated carbon adsorption and caustic regeneration. Further studies of phenol adsorption on an engineering scale are recommended to determine the ultimate service life of activated carbon by extending the number of cycles run, to further optimize the regeneration process by studying countercurrent regeneration, and to determine carbon performance at higher flow rates and higher temperatures.

The same activated carbon technique of byproduct recovery is a satisfactory method for dealing with waste brines contaminated with acetic acid. The process requires low temperatures and flow rates. Better methods of treating byproducts containing acetic acid and other similar small organic molecules are needed that are operable over wider temperature ranges.

SECTION III

INTRODUCTION

Waste brines contaminated with organic materials are one of the major disposal problems in the chemical industry. Brines are a particular concern because the standard biological treatment plants are usually upset by the high salt level which hinders biological oxidation. The brine also passes through the treatment plant and becomes a dissolved solids addition to the receiving waters, thereby, affecting the uses to which the water can be put. At present, brines are disposed of in three ways. They are discharged into seawater, if convenient, or diluted and discharged into fresh water streams, or injected into disposal wells. Discharge into fresh or seawater is coming into increasing scrutiny by pollution control organizations, resulting in more stringent requirements for the brine discharge. Disposal wells are a third way to handle briney wastes, especially for inland plants, but they require suitable geology, and a properly installed, operated, and monitored disposal well is expensive. In addition, subsurface disposal of organically contaminated brines should not be considered a satisfactory long-term solution to the waste disposal problems of the chemical industry.

Chlorine and caustic soda plants all over the United States use salt brine as a raw material source. Thus, it seems logical and feasible to use waste brines as raw material sources after suitable removal of contaminants.

As the beginning of a program on contaminated brine reuse, the waste brine from a phenol manufacturing facility was selected for demonstration studies. The waste brine from this plant is about the same strength as the raw production brine used in the chlorine-caustic soda cells. It is thus an obvious candidate for recycle to chlorine-caustic soda production. The nominal composition of this waste brine is:

Sodium chloride, %	18
Phenol, mg/l	150-750
Sodium acetate, mg/l	1400-2000
pH	8
Temperature, °C	108
Insolubles, $Fe(OH)_3$, ppm	<1 to 10

It also contains benzene and acetone, which have been reduced to low levels by steam stripping.

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Range finding experiments to test the effects of phenol and sodium acetate on a 6 ampere laboratory scale diaphragm-type chlorine cell had shown that 200 mg/l of phenol is unacceptable, but sodium acetate may be acceptable when judged by their effect on the operation of the diaphragm cell. Phenol is destroyed in the electrolytic cell and therefore affects current efficiency, whereas, acetate passes through the chlorine cell intact. Therefore, it was concluded that substantial recycle of such a contaminated brine requires organic removal to preclude problems in chlorine production and caustic soda finishing.

In considering processes to remove phenol and sodium acetate, each organic component was examined separately. Research showed that phenol can be removed from brines by stripping, solvent extraction, and adsorption. Steam stripping requires a good distillation column and a high heat load. Solvent extraction requires an efficient contactor and solvent recovery. Adsorption can be on activated carbon or other adsorbents, but activated carbon had a much greater capacity for phenol than any other adsorbent.

In order to remove sodium acetate from an aqueous system, it is necessary to convert it to acetic acid by acidifying to at least pH 3. The following processes were examined without success: solvent extraction, azeotropic distillation, and extractive distillation. Acetic acid was adsorbable on activated carbon at relatively low but still practical loadings.

In view of the failures and problems of other unit operations considered, adsorption on activated carbon became the only practical approach for purifying this byproduct brine. However, the key to the successful use of the unique adsorptive properties of activated carbon in industrial waste treatment is the regeneration process.

Industrial wastes, having organic concentrations orders of magnitude greater than municipal wastes, saturate carbon much more quickly. Cycle times are short, carbon requirements are high. Thermal regeneration, with its 5 to 15% carbon loss per regeneration, means the carbon is replaced every 7 to 20 cycles. For industrial wastes, this cost becomes prohibitive. What is needed are regeneration processes giving a much longer, useful carbon life.

Further research defined the activated carbon process as follows: phenol is removed from the brine at pH 7; the brine is then acidified with HCl to pH 3 and passed through another carbon bed to remove acetic acid. As each carbon bed becomes saturated, it is regenerated by chemical desorption of the organics with caustic soda solution. This research and development grant for the demonstration of the recondition and reuse of this organically contaminated brine had the following project objectives:

a) Develop and demonstrate a chemical-adsorption process for the treatment of process wastewater from a phenol manufacturing plant.

b) Demonstrate the requirements for byproduct recovery from the subject wastewater, which will include the net recovery of both organic and inorganic pollutants.

c) Demonstrate wastewater reuse on an engineering scale.

d) Research and develop methods for: 1) the regeneration of adsorption materials to be used in the proposed process, and 2) establishing requirements and limitations on the use of renovated brine wastewater for chlorine-caustic production.

The project was to be completed within a period of two years (beginning June 30, 1969) in three major phases: Phase I - Design and Engineering (6 months), Phase II - Construction (6 months), and Phase III - Operation of the Demonstration Plant (12 months).

The purpose of the Phase III operational portion was to demonstrate plant operability on an engineering scale and to define and optimize cost-sensitive operating parameters for the activated carbon adsorption process for removing phenol and acetic acid from a sodium chloride brine. Removal of these organic contaminants must be sufficient to allow recycle of the brine to chlorine-caustic soda production. The level of contaminants in the adsorption plant effluent depends on flow rate, contact time, temperature, pH, and the conditions of the carbon after regeneration. Costs are also affected by the above as well as by the carbon bed life.

Operating conditions which most affect the adsorption and regeneration of each bed were defined first in a supporting research program. The Demonstration Plant then operated at these conditions to provide data on an engineering scale for determination of performance and costs. The supporting research studies also studied methods of recovering acetic acid from the regenerant and investigated the physical properties of the activated carbons for correlation with plant performance.

In order to determine precisely, on a semi-commercial scale, the effects of the reconditioned brine on the manufacture of chlorine and caustic soda in diaphragm-type electrolytic cells, two specially instrumented 2660-amp test cells were operated in the chlorine production area during Phase III. These test cells were smaller than production cells but large enough to supply reliable pilot plant data. One cell was fed seven tenths of a liter per minute of treated brine from the Demonstration Plant. The second test cell operated on pure brine to serve as a control for comparison.

SECTION IV

DESIGN OF DEMONSTRATION PLANT

The waste brine purification facility was designed to remove the organic components from stripped Phenol Plant brine in order to recycle the 18% NaCl brine to Chlorine-Caustic Production. This Demonstration Plant was designed to process 100 gal/min of stripped feed brine of the following nominal composition:

NaCl	- 18%
Phenol	- 200 mg/l
Benzene	- 10 ppm
Acetone	- 10 ppm
Sodium Acetate	- 1400 mg/l

It was also designed to handle traces of finely divided inorganic sludge, typically iron hydroxide. The design called for a product brine containing <5 mg/l phenol and approximately 140 mg/l sodium acetate, when operated at temperature of 30°C. The NaCl concentration would not be changed in this facility and would be the same as the feed brine (nominally 18%).

The plant was located outdoors in an area across the street from the Phenol Production Plant. A control house was built adjacent to the plant for instrumentation and plant utilities. Research pool operators were used to man the Demonstration Plant 24 hr per day, 7 days per week.

Unit ratios for design were

	Peak Demand Rate	Avg. Use
Brine	200 gal/min	100 gal/min
Lake water	100 gal/min	0.216 gal/gal
Caustic as 100% NaOH	45 lb/min	0.162 lb/gal
HCl as 100%	30 lb/min	0.0018 lb/gal
Spent Phenate Regenerant	100 gal/min	0.10 gal/gal

Utilities

	Peak Demand Rate	Avg. Use
Electrical	125 KW	0.016 KWH/gal
Steam (150 psig)	7,000 lb/hr	0.19 lb/gal

The plant should purify 100 gal/min of waste phenate brine for use in the chlorine cells. This 100 gal/min of brine would not go to subsurface disposal. Ten gal/min of spent acetate regenerant are to be sent to the disposal wells giving a net reduction of 90 gal/min to subsurface disposal.

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Laboratory data as well as the literature indicated that 2 gal/min/sq ft superficial velocity was a reasonable condition for design of carbon adsorbers. These rates give pressure drops of about 2" water per foot of carbon on a clean bed. The question of height of bed was decided on the basis of loading of the least well adsorbed impurity. We could expect a loading of 0.05 lb acetic acid/lb carbon at our operating conditions and this would result in saturation of an 18 ft bed in about 24 hours. The design specified two carbon columns for phenol adsorption and two columns for acetic acid adsorption. They were operated downflow in series except when one was off-line for regeneration.

There is a definite cost advantage to buying multiple equipment of the same design so the phenol adsorption towers were designed to be the same size as the acetic acid towers. This results in a much longer adsorption cycle for phenol. At a loading of 0.15 lb phenol/lb carbon and a feed concentration of about 300 mg/l phenol, six-day cycles could be expected with an 8' bed height. It was decided to buy vessels that had a potential carbon height of 20 ft, giving the flexibility to load any quantity of carbon in order to attain a reasonable number of cycles during the grant operating period.

Carbon vendors advised as to the galvanic type corrosion of steel in contact with carbon beds. This, coupled with our corrosive solutions, led us to the choice of rubber-lined steel as material of construction.

Regeneration was also designed to be carried out downflow, or cocurrent to adsorption. This simplified the piping and carbon support designs. The bed supports were simple in design. Structural support was furnished by channels welded to the vessel and then rubber coated. Perforated steel plates coated with vinyl plastisol were laid on the channels. Then a polypropylene filter cloth that could retain 20-40 mesh carbon was laid over the perforated plates. Sealing to the vessel sides was with a silicone RTV sealant.

It was recognized from lab data that careful pH control was essential to adsorption of acetic acid. Therefore, it was decided to use a stirred tank with one hour residence time (6000 gal) and continuous recirculation of a sample through an inline pH sensing device. The pH sensor was to operate a control valve that regulates the HCl addition rate. Operating data have proven that this is an excellent system controlling at pH 3.0 ± 0.1 pH unit.

The treated brine neutralizing tank was sized at 1800 gallons because the pH control is not so critical. Since the pipeline to the Chlorine Plant was a steel pipeline, the purified brine effluent from the acetic acid adsorbers at pH 4 had to be neutralized to the pH range of 7.5-8.5.

The clarifier was designed on the basis of settling rates attained on Phenol Plant brine with the addition of Purifloc® A-23 flocculant at 0.2 ppm. This resulted in the vessel dimensions of 30 ft dia by 10 ft high with a standard overflow weir.

The tank volumes were selected on the basis of projected use rates in the case of reagents and accumulation rates for process vessels. Caustic and HCl storage were sized to be refilled once a shift. Lake water was contained in a surge tank of 1000 gal capacity to stabilize a repressurized system. Phenate regenerant was to be continuously pumped at 50 gpm so 750 gallon was an adequate size to give a 15 minute surge capacity. Acetate regenerant was to be recycled and reused, and based on the regenerant volume projected, a 12,000 gallon tank was selected.

The materials of construction used in the Demonstration Plant were in the following categories:

Service	Material
18% NaCl Brine above 80°C, pH 7-9	
pipe	Sched 80 steel
pumps	Ductile Cast Iron
valves	Forged Steel
heat exchanger	Forged Steel
18% NaCl Brine below 80°C, pH 6-9	
pipe	Sched 40 steel
pumps	Ductile Cast Iron
valves	Forged Steel
18% NaCl Brine, pH 2-3	
tanks	Butyl Rubber-Lined Steel
agitators	Butyl Rubber-Lined Steel
pipe	Propylene-Lined Steel
pumps	Polypropylene-Lined Steel
Sodium Hydroxide Sol'ns, 4%-30%	
pipe	Sched 40 Steel
pumps	Ductile Cast Iron
agitators	Forged Steel
Hydrochloric Acid Sol'ns 17-36%	
pipe	Polypropylene-Lined Steel
pumps	Polypropylene-Lined Steel

Standard design practices were used for foundations, vessel supports, pipe supports, etc. These standards have been developed by long term experience in construction of chemical processing plants.

Complete engineering details and drawings of the Demonstration Plant have been recorded in the Design and Engineering Report submitted to the Environmental Protection Agency. The design and construction of the facility was done from June 30, 1969, to August 27, 1970. Construction was done from February 1970 through August 27 by outside contractors with client inspection as required. Photographs of the completed facility are shown in Figures 1 and 2. Figure 1 shows the activated carbon adsorption columns and the control house. Figure 2 is an overall photograph of the Demonstration Plant. The concrete clarifier is seen on the left, raw materials tankage and the air cooler in the middle foreground, the Dempster stations and control house on the right. In the far background can be seen portions of the Phenol Plant where the brine originates.

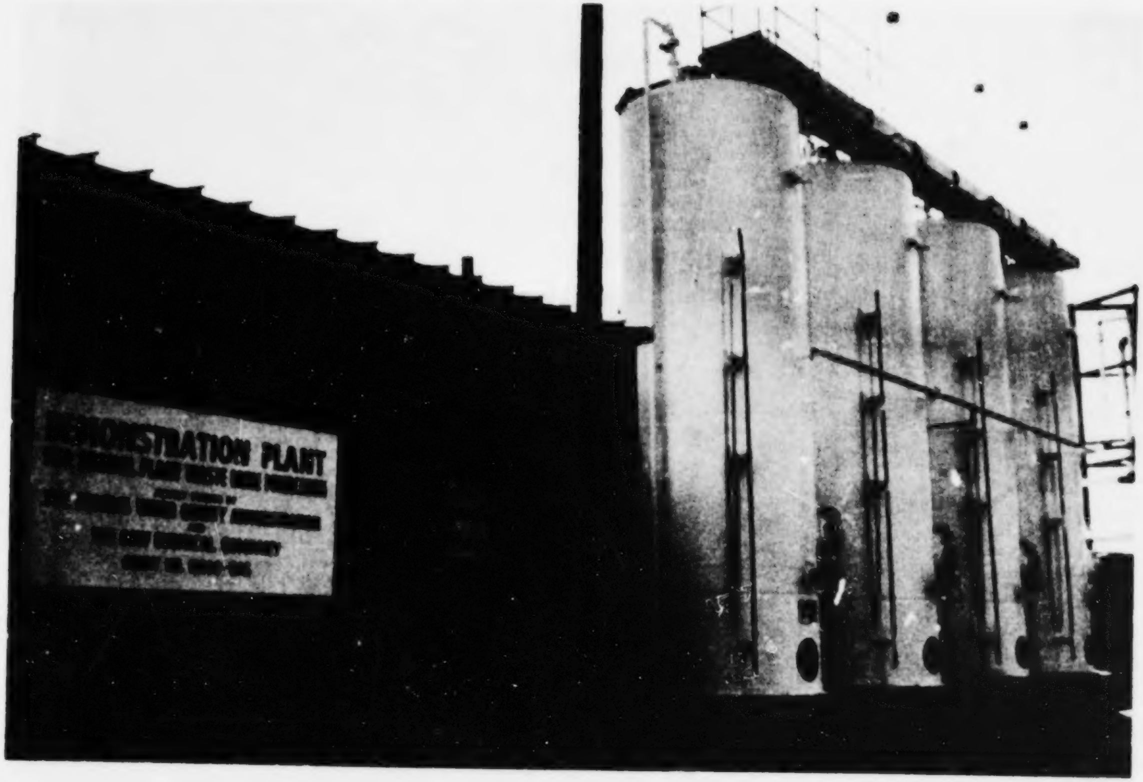

DEMONSTRATION PLANT

Figure 1
PHOTOGRAPH OF DEMONSTRATION PLANT ADSORBERS AND CONTROL BUILDING

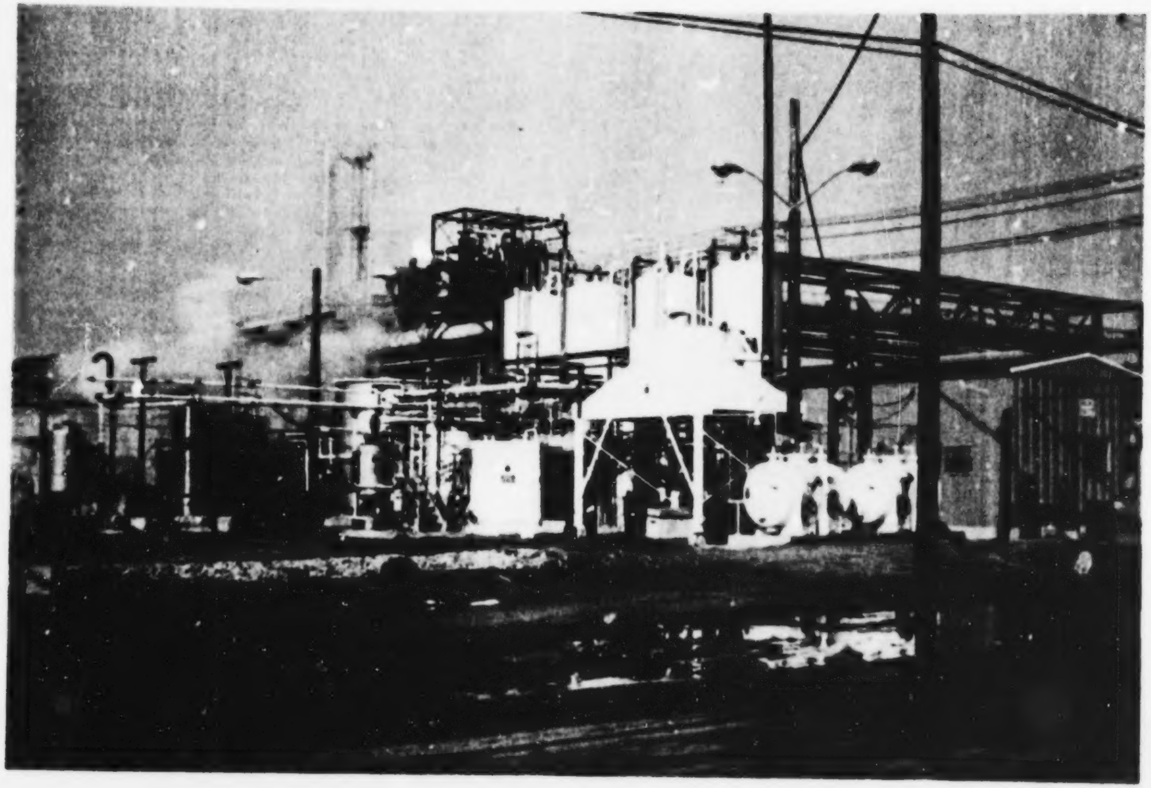


Figure 2
PHOTOGRAPH OF ENTIRE DEMONSTRATION PLANT

SECTION V

DEMONSTRATION PLANT OPERATION

After startup in late August 1970, the Demonstration Plant was operated for thirteen months, during which time over 23 million gallons of the actual byproduct brine from the Phenol Manufacturing Plant was purified. During this period of time, the conditions under which the plant was run were varied to determine the effects on certain variables on both the adsorption and the regeneration processes. In addition, the plant operation also experienced both the variations in conditions caused by a complete annual cycle of Central Michigan weather and also the variations that are caused by the operation and misoperation of the phenol process equipment.

The quality of the feed brine received from the Phenol Plant was highly variable. From the beginning, the specification on feed brine analysis used as the design basis for the plant was too restrictive. Phenol, acetone and benzene concentration were frequently higher than the specifications. Acetic acid concentration did not vary as greatly or rapidly as the concentration of these other organics. The feed brine specifications were eventually adjusted to accommodate the real capabilities of the Phenol Plant equipment, especially the brine stripper. The acceptable maximum concentrations were raised to 1500 mg/l for phenol, 50 microliters/l for acetone, and 15 microliters/l for benzene. The incoming feed brine was sampled every two hours to monitor the concentration of these organics. Failure to consistently meet feed brine specifications was caused by two major problems.

The first problem was the inability of the Phenol Plant to meet the specified organic contaminant level in the stripped brine. It was necessary to improve the steam stripping operation to hold volatile organics (acetone and benzene) at the required levels. Another problem was upsets in the extractor operation which resulted in intolerable phenol levels above 2000 ppm. The correction to this problem was more precise pH control and increased solvent to brine ratios in the extractors in the Phenol Plant. For effective phenol extraction and adsorption, the pH must be less than 9. Sufficient contact between the phenol bearing brine and the benzene extractant must be maintained for good extraction. Toward the end of the operating period both problems had been corrected, and throughputs of 130-140 gpm of quality brine were being attained. These problems serve to illustrate the variability of feed quality with which an industrial waste treatment process must be designed to cope.

The second operating problem was the inability of the Chlor-Alkali Plant to accept the purified 18% NaCl brine when it was short of solid NaCl to saturate the brine. When the Chlor-Alkali Plant could not saturate purified brine, the Demonstration Plant was operated to collect data, and the product brine was pumped underground for disposal.

The adsorption process shown schematically in Figure 3 is operated as follows:

> The feed brine to the unit is received from the stripping still at the Phenol Plant at 108°C. Purifloc A-23 flocculant is added to the hot brine, and the insoluble flocs are allowed to settle in the clarifier. The clarifier overflow is cooled in an air cooled exchanger to the temperature selected for study in the range of 30 to 70°C. Brine is pumped at a controlled flow rate down through two activated carbon beds in series for removal of phenol. The brine, after passing through phenol adsorption, is acidified to a pH of 3 by adding HCl on pH control. The acidified brine is then pumped at a controlled flow rate down through two activated carbon beds in series for removal of acetic acid. The treated brine is collected in a surge tank where it is neutralized by addition of NaOH on pH control. The brine is pumped to the brine treating plant in the Chlor-Alkali complex. A continuous sample flow of the treated brine stream is collected in a Dempster tank for transport to the chlorine test cells. About half-way through the operational phase, it was concluded that more brine could be processed through the phenol adsorbers, but that the capacity of the acetate adsorbers would be exceeded, especially as operating temperatures rose in the summer. In order to process more brine through the phenol adsorbers but have only a portion of the dephenolated brine go to the acetic acid adsorbers, a by-pass and control system (shown in Figure 3) was installed to divert to the treated brine tank any brine not pumped to the acetic acid adsorbers. This allowed operation at rates of to 140 gal/min, which was the limit of the Phenol Plant stripper, through the phenol adsorbers. The flow to the acetic acid adsorbers was restricted to 60-80 gal/min. This change occurred at Cycle No. 70 on the acetic acid absorbers.

Regeneration of the phenol beds, shown schematically in Figure 4, is done as follows:

> When the first phenol bed becomes saturated as monitored by outlet phenol concentration approaching the inlet concentration, it is taken off line for regeneration; the second bed continues to process feed brine. Twenty-seven percent plant caustic is diluted with filtered lake water to 4% by use of a flow ratio controller to serve as re-

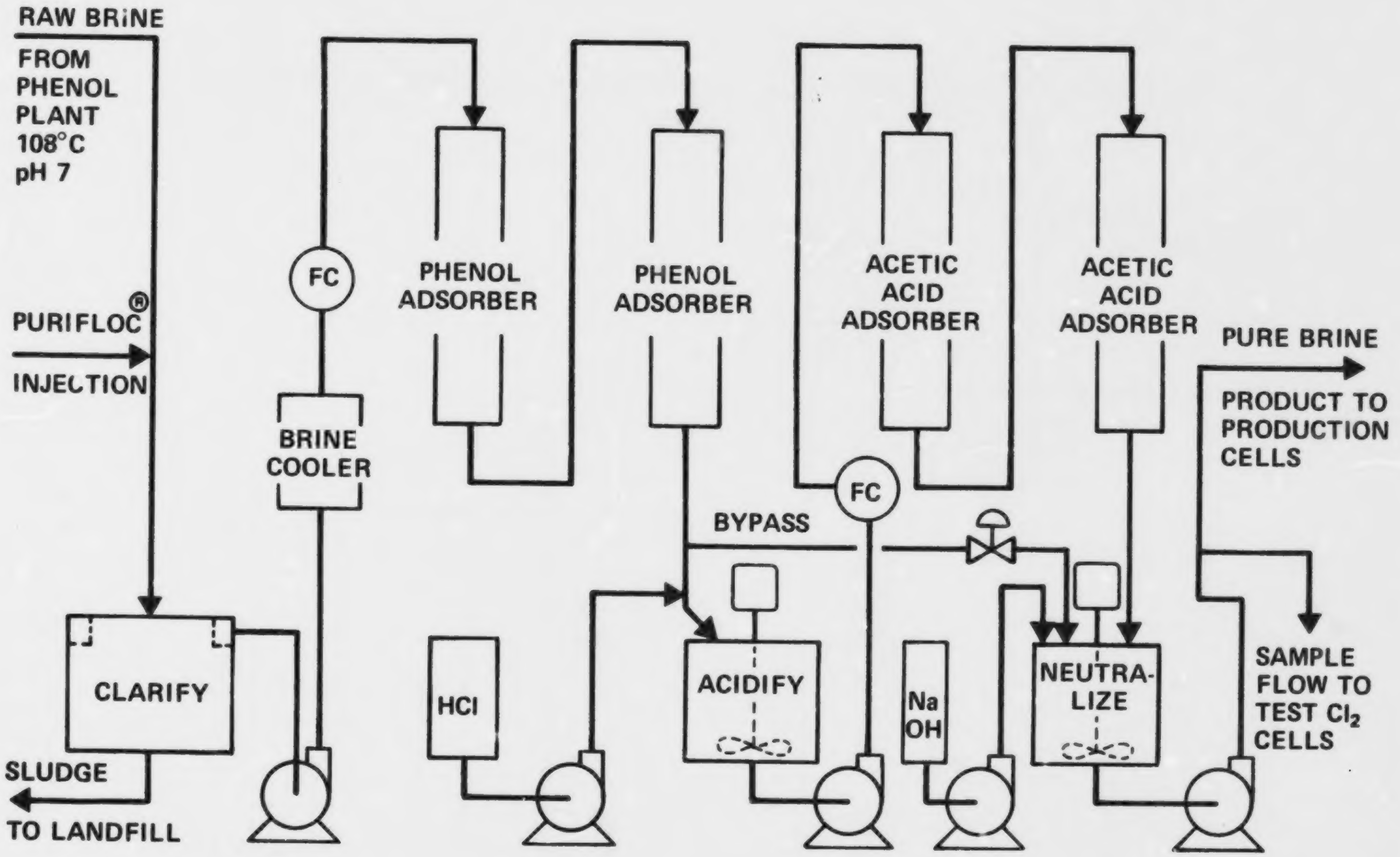

RAW BRINE
FROM PHENOL PLANT 108°C pH 7
PURIFLOC®
INJECTION
CLARIFY
SLUDGE
TO LANDFILL
FC
BRINE COOLER
PHENOL ADSORBER
PHENOL ADSORBER
ACETIC ACID ADSORBER
ACETIC ACID ADSORBER
FC
BYPASS
HCl
ACIDIFY
Na OH
NEUTRA-LIZE
PURE BRINE
PRODUCT TO PRODUCTION CELLS
SAMPLE FLOW TO TEST Cl2 CELLS

Figure 3
SCHEMATIC FLOWSHEET OF ADSORPTION PROCESS

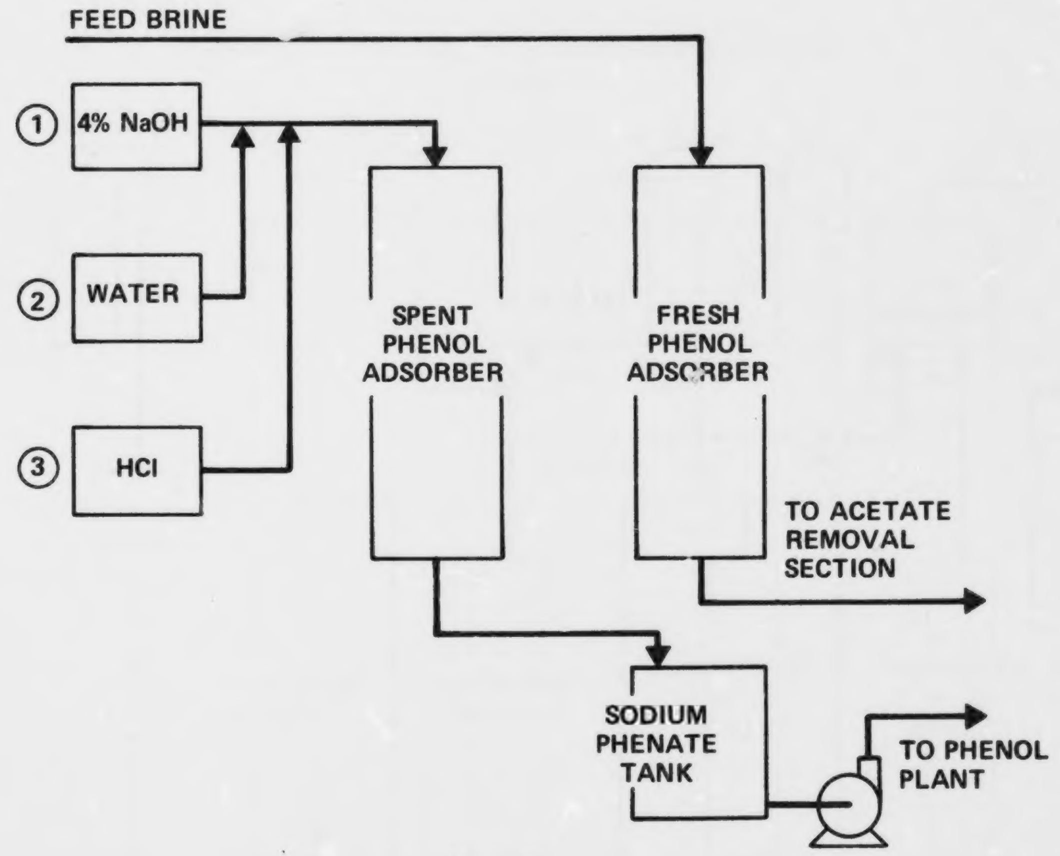

FEED BRINE
① 4% NaOH
② WATER
③ HCl
SPENT PHENOL ADSORBER
FRESH PHENOL ADSORBER
TO ACETATE REMOVAL SECTION
SODIUM PHENATE TANK
TO PHENOL PLANT

Figure 4

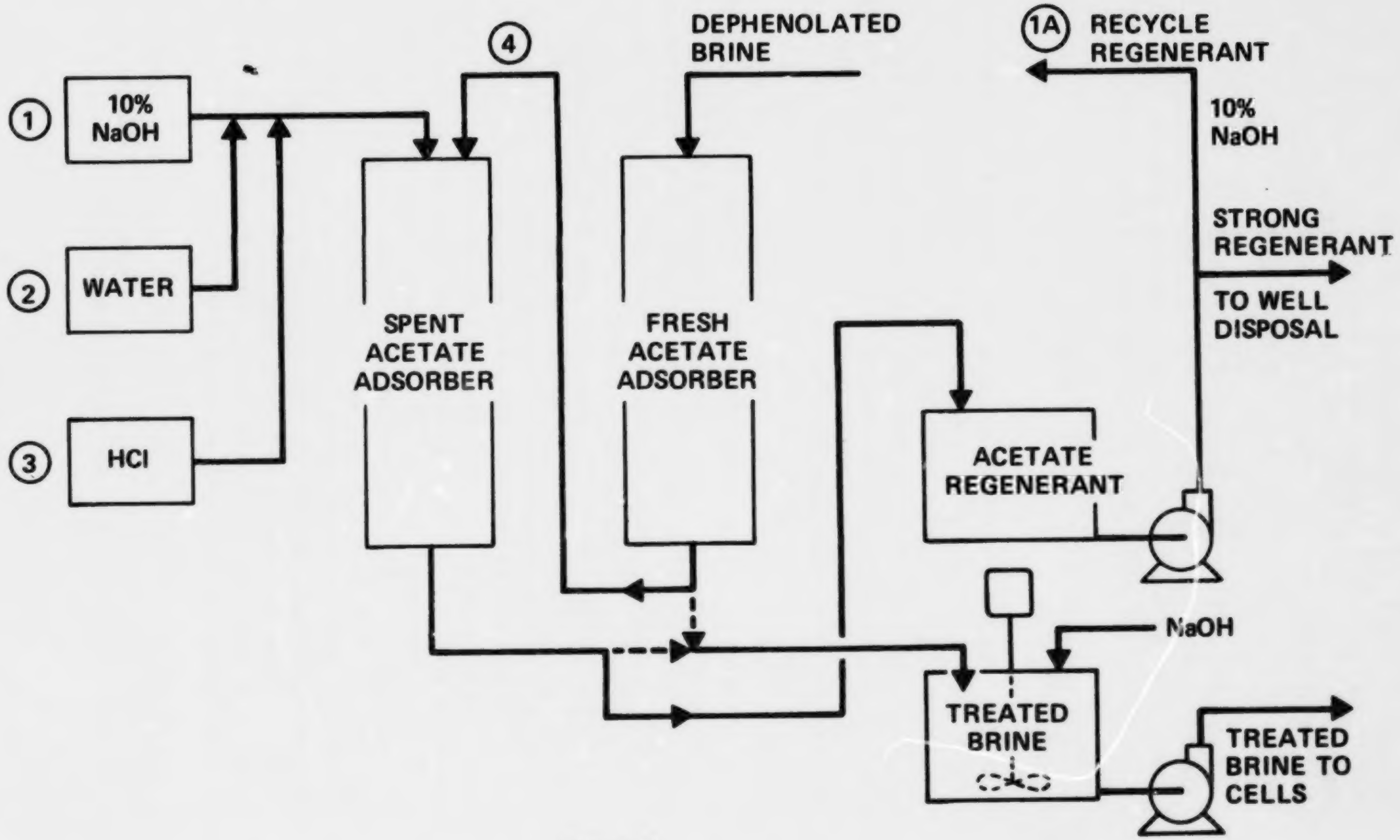
SCHEMATIC FLOWSHEET OF PHENOL COLUMN REGENERATION PROCESS

> generant solution. The regenerant is pumped on flow control down through the bed at 1/3 to 1/2 the adsorption flow rate. The displaced feed brine is pumped to the disposal well line to prevent adding salt to the phenate regenerant. All regenerant solution but the initial displaced brine is collected in the phenate regenerant tank and returned to the Phenol Plant as dilute caustic for their use. In order to achieve good effluent quality in the subsequent adsorption cycle, regeneration must be continued until the level of phenol in the column effluent reaches 500 mg/l. The regenerated bed is put on line down stream from the partially spent bed, and the cycle is repeated as the beds saturate alternately.

Regeneration of acetate beds, shown schematically in Figure 5, is done as follows:

> When one acetate bed becomes saturated as monitored by outlet acetic acid concentration approaching the inlet concentration, this bed is taken off line for regeneration; the second bed continues to process feed brine. A sequence of regeneration steps using caustic are then performed to optimize the concentration of sodium acetate in the regenerant and minimize the volume of regenerant. Two methods were used differing only in the caustic regenerant make-up. The first method was to make up 10% NaOH solution by mixing the 27% caustic supply with water in a flow system. The second method utilized the weak regenerant at the end of the cycle as a dilution source, and 27% caustic was added to the regenerant tank to give a 10% caustic solution. After the caustic was pumped downflow into the bed, the carbon bed was sequentially washed with water and acidified with HCl to prepare it for adsorption service. The regenerant solution that has a high acetate concentration was pumped to the disposal well system. In the first method, the regenerated bed was placed in adsorption service when the pH of the effluent dropped below 3, and all regenerant was pumped underground. In the second method, regenerant was pumped out until the sodium acetate concentration in the regenerant sample was less than 2 g/l and then the weak regenerant was saved as makeup solution for the next cycle. The regenerated bed was put on line downstream from the partially spent bed, and the cycle was repeated as the beds saturated alternately.

Simple operating control analyses were done by Research Operators operating the adsorption facility. Complex analyses were performed by the Analytical Services Laboratories.



1
10% NaOH
2
WATER
3
HCl
4
SPENT ACETATE ADSORBER
DEPHENOLATED BRINE
FRESH ACETATE ADSORBER
1A
RECYCLE REGENERANT
10% NaOH
STRONG REGENERANT
TO WELL DISPOSAL
ACETATE REGENERANT
NaOH
TREATED BRINE
TREATED BRINE TO CELLS

Figure 5
SCHEMATIC FLOWSHEET OF ACETIC ACID COLUMN REGENERATION PROCESS

Carbon Selection

As determined in the laboratory studies, commercially available carbons do not show much difference towards phenol selectivity. The principal basis for selection of eligible suppliers was the initial capacity or loading for acetic acid. Bids were solicited on three grades of carbon: Witco 718, 12 x 30 mesh; Westvaco Nuchar WV-G, 12 x 40 mesh; and Pittsburgh CAL, 12 x 40 mesh. Witco petroleum coke base carbon, and Nuchar bituminous coal base carbon, were selected as suppliers of 1200 cu ft of carbon each. The original plan was to load 800 cu ft of each in the acetic acid adsorbers, and only 1/2-fill the phenol adsorbers with 400 cu ft of each. This arrangement would provide a long term use comparison of two different types of carbon.

Startup

After check-out of the mechanical aspects of the system using water, carbon loading began in late August. A jet eductor was used to suck dry carbon from a hopper into a 100 gpm recirculating water stream and lift it to the top of the water-filled adsorption column. The carbon was allowed to fill the column by free-fall through the water. Water flow was also downflow through the support screen, so no backwashing of fines from the carbon was accomplished. The phenol adsorbers were filled to 8' height and the acetic acid adsorbers were filled with the balance of the initial carbon shipments. They had ~18' of carbon at the beginning. Brine treatment commenced in late August, and shortly thereafter, the appearance of insoluble hydroxides in the treated brine made it necessary to stop operation after a few hours and acid-wash the carbon. This was done by circulating acid brine through the columns, and after neutralization, back to the clarifier for solids removal.

The first 2 cycles on the Witco 718 phenol adsorption column and the first cycle on the Nuchar WV-G phenol column were run with the 8' of carbon bed height. The operational problems of getting plug-flow of regenerant, with a column only half-full of carbon, were such that it was decided to fill the columns completely. This was accomplished in early November. Similar problems in achieving plug-flow of regenerant were also experienced with the nearly-full acetic acid adsorbers, so they were also filled up with carbon. This brought the amount of carbon in each adsorber to the following weights:

Witco 718 phenol adsorber : 27,500 lb
Nuchar WV-G phenol adsorber : 26,750 lb
Witco 718 acetic acid adsorber : 29,500 lb
Nuchar WV-G acetic acid adsorber: 26,600 lb

All four columns then contained 19' of carbon. This increased quantity of carbon in each phenol adsorption column has had the effect of more than doubling the length of the cycle time of each column. It was on the basis of this carbon column configuration that the performance of the Demonstration Plant was evaluated.

SECTION VI

DEMONSTRATION PLANT PERFORMANCE

As a result of processing 23 million gallons of brine during the one year operating period, 14 cycles for phenol adsorption and regeneration and 105 cycles for acetate adsorption and regeneration for each type of carbon were completed.

The degree of freedom in choosing temperature variables for adsorption were regulated by the air-cooled heat exchanger. For a given ambient air temperature, the adsorption temperature of the carbon columns was a function of flow rate. The system was actually operated at flow rates ranging from 50-140 gal/min and at temperatures ranging from 15° to 70°C. With an empty bed volume of 7100 gal and a void volume of 75%, the range of residence time for the above flow rates was 100 min to 40 min.

Phenol Adsorption and Regeneration

The quality of the effluent from the phenol adsorbers under stable operating conditions after several cycles of cocurrent regeneration ranged in phenol concentration from 0.5 to 4.0 mg/l. The higher values are believed to have resulted from incomplete regeneration of the column. The phenol adsorption system, after 13 cycles of adsorption and regeneration, produced effluent brine containing 0.7 mg phenol/l when treating 140 gal/min of brine containing 300 mg phenol/l at 70°C. It can be concluded that a properly regenerated carbon system can produce an effluent containing <1.0 mg phenol/l with good carbon capacity at flow rates up to 2.8 gal/min/sq ft and temperatures up to 70°C.

Two typical phenol adsorption breakthrough curves at 105-110 gal/min and 60°C for each type of carbon are presented in Figures 6 and 7. These data were collected when the flow rate through the adsorbers remained fairly constant throughout the cycle. The phenol concentration in the feed was not uniform; these curves illustrate the feed concentration fluctuations which were encountered. In both of these cycles, the effluent from the columns was less than 1 mg/l until breakthrough. Figure 7 also serves to illustrate other pertinent points. The effluent from the carbon column after being placed in service following regeneration is not low. This can occur if the regeneration is not complete. The shape of the breakthrough curve is also noteworthy. Breakthrough occurs when the column is ~40% loaded and the column slowly begins to pass ~20 mg/l phenol as the column is treating strong feed (>800 ppm phenol). However, once the feed compo-

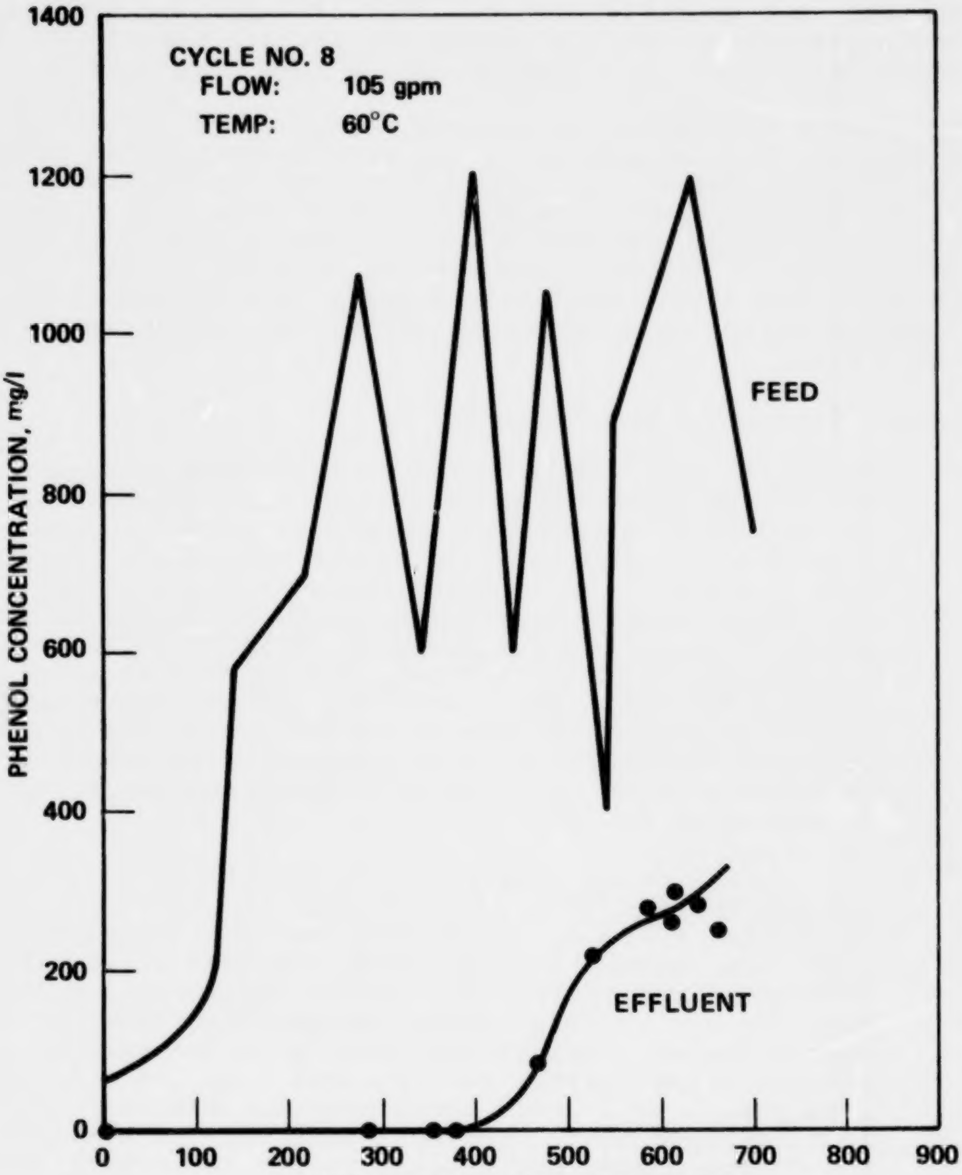


Figure 6
BREAKTHROUGH CURVE FOR NUCHAR WV-G PHENOL ADSORBER, CYCLE NO. 8

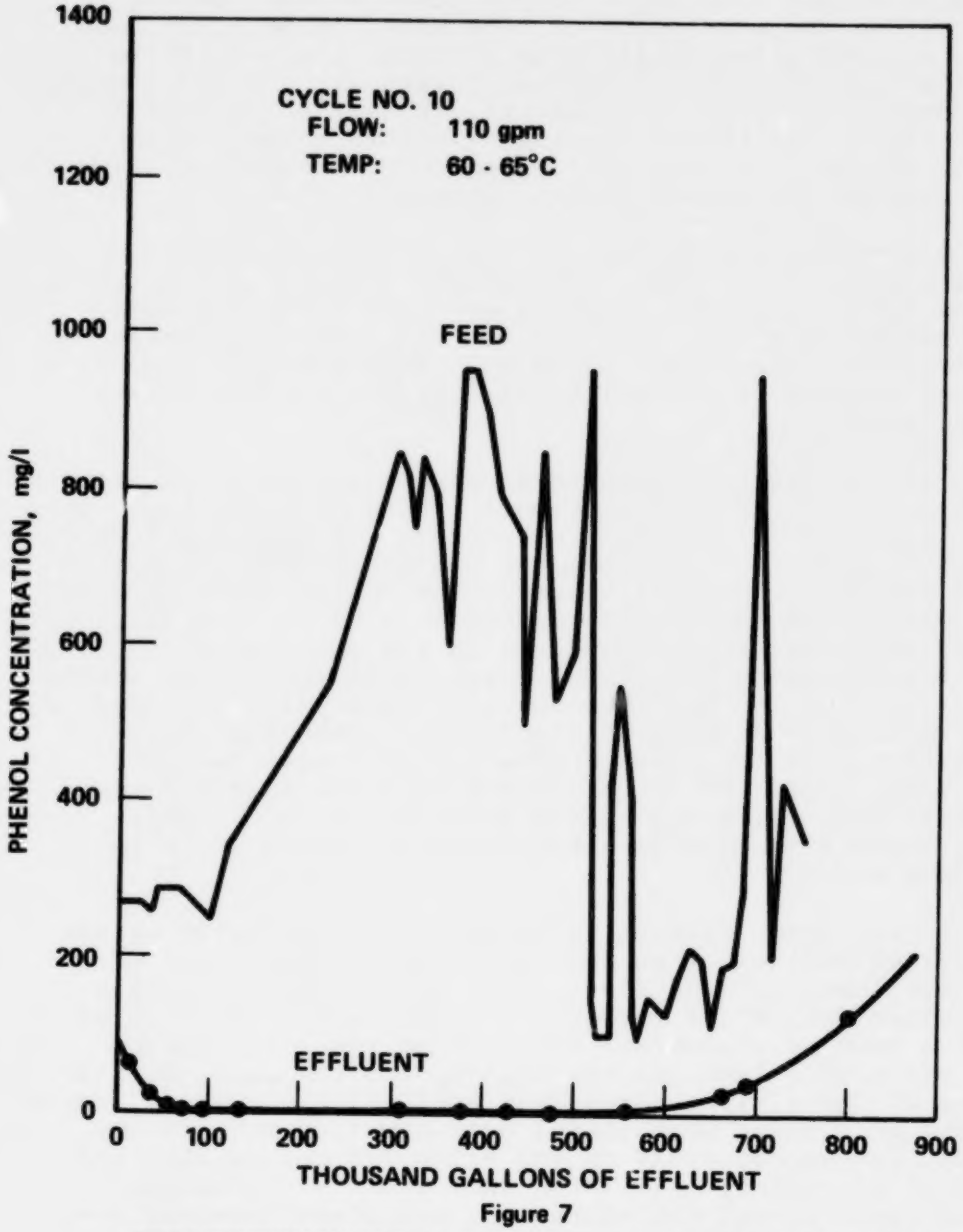


Figure 7

BREAKTHROUGH CURVE FOR WITCO 718 PHENOL ADSORBER, CYCLE NO. 10

sition dropped down, the column was able to hold its own until it saturated. The loading was calculated from these graphs for comparison with equilibrium data and regeneration data.

Because of the long phenol cycle time periods, during which time the conditions of flow rate, temperature, and feed concentration varied considerably, the calculation of loadings from the adsorption curves was not an accurate approach. In order to track changes in the adsorptive capacity of the phenol adsorbers with repeated regeneration cycles, the loading for each cycle was measured by integrating the sodium phenate desorption curve.

The regeneration data for all cycles are summarized in Tables 1 and 2 for Witco 718 and Nuchar WV-G, respectively. These tables list the regeneration conditions employed, the amount of phenol removed, and the effects observed on the total regenerant effluent. From the amount of phenol removed, an effective loading for each cycle was calculated.

Most of the regenerations were carried out with ~30 gal/min. (0.6 gal/min/sq ft) of 4% caustic, because equilibrium data had suggested the optimum to be around 4% and slow flow rates do provide conditions for maximum phenol desorption with minimum regenerant volume. The region below 4% NaOH was not tested because of concern that sufficient alkalinity would not exist for raising the pH and reacting with phenol. The rate at which the Phenol Plant could accept the regenerant recycle in their process also restricted the flow rate options. As seen in the Tables, there were a few occasions when the caustic soda strength and flow rate did vary. The chief regeneration variable examined was temperature, which was varied from 15° to 65°C. Data from 3 regenerations were misplaced or judged to be in obvious error.

One of the first effects to be noted in the Tables is the effect of bed height on the regenerant effluent and effective loading. The first cycle on each carbon column contained only 8' of carbon. A comparison of 4% NaOH vs 14-19% NaOH as regenerant was made on the first cycle. The effluent volume and the loading was the same, but the shape of the elution curves was much different as evidenced by the much lower peak phenol concentration with 14-19% NaOH. The second cycle on the Witco 718 column also had only 8' of carbon. All three indicators - regenerant volume, peak phenol concentration, and phenol removed were worse as compared to the first cycle.

It was at this point that both carbon columns were filled with carbon to 19' height to facilitate plug-flow during

TABLE 1

SUMMARY OF PHENOL REGENERATION DATA ON WITCO 718 CARBON

Cycle No.	Bed Height, ft.	Regenerant						Carbon Loading lb phenol/lb
		Feed			Effluent			
		% NaOH	Flow, gpm	Temp., °C	M gal.	peak phenol conc., mg/l	lb phenol	
1	8	4	36	25	29	50,000	1660	0.138
2	8	4	25	15	56	20,000	740	0.062
3	19	4/15	30/5	15/32	110	61,000	6550	0.250
4	19	4	33	30	108	61,000	5820	0.220
5	19	4	30	50		bad data		
6	19	4	30	55	60	98,000	6160	0.233
7	19	4	30		48	62,000	4600	0.174
8	19	4	30				6000	0.210
9	19	4	30/12	60/50	61	62,000	5900	0.207
10	19	4	30	55	54	37,000	3865	0.142
11	19	4	30	60	68	46,000	3990	0.145
12	19	4	30	55	54	58,000	3995	0.145
13	19	4	30	50-60	45	57,000	6200	0.236
14	19	4/12	30/17	50-60	62	42,500	4640	0.175

TABLE 2

SUMMARY OF PHENOL REGENERATION DATA ON NUCHAR WV-G COLUMN

Cycle No.	Bed Height, ft.	Regenerant						Carbon Loading lb phenol/lb
		Feed			Effluent			
		% NaOH	Flow, gpm	Temp., °C	M gal.	peak phenol conc., mg/l	lb phenol	
1	8	14-19	15	25	29	10,500	1300	0.145
2	19	4	30	10	140	59,000	5700	0.226
3	19	4	33	10	140	42,000	4420	0.176
4	19	4	30	30	135	49,000	4180	0.165
5	19	4	30	55	66	64,500	3900	0.154
6	19	4	25	60	72	88,000	4450	0.175
7	19	4	30				4500	0.177
8	19	8/4	30	55	72	34,000	3100	0.116
9	19	4	30	55	52	69,000	4100	0.153
10	19	4	30	25/60	54	61,500	3350	0.125
11	19	4	30	65	63	48,000	3090	0.116
12	19	3-11	6/30	60	65	64,000	4930	0.184
13	19	7	30	60	80	21,000*	2510*	0.10*
14	19	18/4	27/32	60	48	58,000	3360	0.125

*Regenerated before saturated

regeneration. From the data collected with this column configuration, three desorption curves have been plotted in Figure 8 to show the effect of temperature. The main temperature effect is on the volume of regenerant, with the higher temperature clearly desorbing phenol down to 500 ppm faster. Thus, high regeneration temperatures become most important to efficient phenol desorption. The observed peak phenol concentration of 98,000 mg/l obtained at 55° was the highest level attained, but no cause could be ascertained. More typical values were around 60,000 mg/l. Another effect on regeneration, that of caustic soda concentration has also been depicted in Figure 8.

The discontinuities in the 15°C curve are due to changes in conditions during the regeneration. They occurred when the dilution water for making 4% caustic stopped and the caustic strength pumped into the column rose to 14-16%. Even though there was a corresponding decrease in flow rate with the attendant increased contact time, the effect of strong caustic on phenol elution is apparent. The higher strength caustic markedly slowed down the rate of desorption. This effect was noted whenever higher caustic strengths were used, as can be seen by comparing the peak phenol concentration and regenerant volume for Nuchar WV-G cycles 8, 11, and 13. On these cycles, the phenol removed was nearly the same, but the cycles using 7-8% NaOH were slower in desorbing. For Cycle No. 14 on Nuchar WV-G, 18% NaOH was used at the beginning and the peak phenol concentration was high, but after 5 hr of regeneration, the caustic strength was lowered to 4%. The result was a definite second phenol peak on the desorption curve of 33,500 ppm. This again showed the advantage of 4% NaOH as regenerant. The volume of regenerant produced with 30 gal/min of 4% NaOH at 55°-65°C ranged from 45,000 gallons to 72,000 gallons, with an average being ~60,000 gallons. This represents 8.5 bed volumes of regenerant.

From the data collected on these 28 cycles of phenol regeneration, the optimum regeneration conditions can be specified. At 30 gpm of 4% NaOH in cocurrent flow and temperatures of 55-65°C, phenol is desorbed from a 19' high carbon column with 60,000 gallons of regenerant being produced. A peak phenol concentration of ~60,000 mg/l can be expected, and the average phenol concentration will be ~10,000 mg/l.

Examination of the loading values calculated by integration of the desorption curves showed no significant deterioration in the effective working capacity of either carbon during the processing of over 23 million gallons of brine.

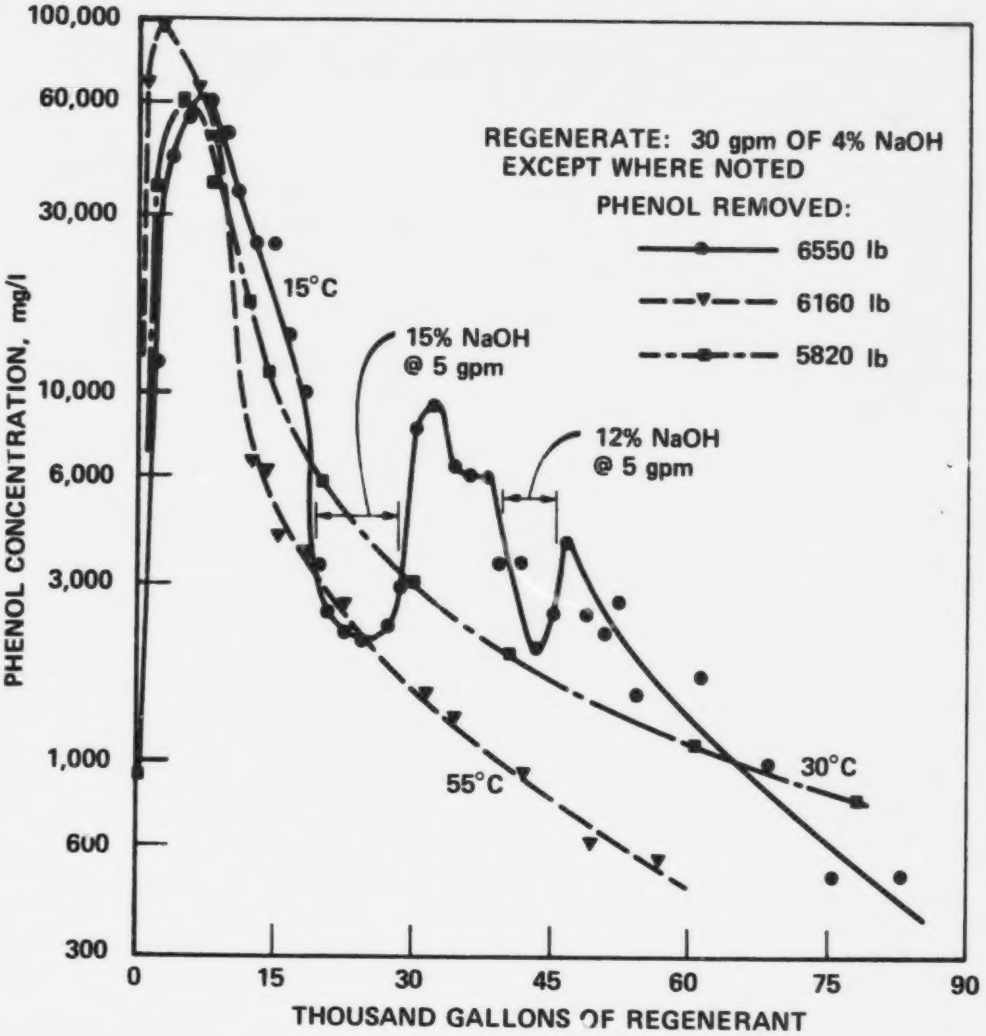


Figure 8

PHENOL DESORPTION CURVES SHOWING EFFECT OF TEMPERATURE AND % CAUSTIC

The variations observed in Tables 1 and 2 are attributed to variable feed compositions and starting regeneration before true saturation of the carbon. The loadings calculated for the two breakthrough curves in Figures 6 and 7 compare favorably with those obtained from the regeneration curves for those cycles. For Cycle No. 8 on Nuchar WV-G, the breakthrough curve loading was 0.144 lb/lb while the phenol removed was 0.116 lb/lb. For Cycle No. 10 on Witco 718, these values were 0.132 lb/lb and 0.140 lb/lb. The loading for these cycles can also be compared with a calculated equilibrium loading obtained from the isotherms in Figures 26, 27, 28, and 29 under Laboratory Studies. The average feed concentration for Cycle No. 8 on Nuchar WV-G was ~800 mg/l; the effective loading from equilibrium data on virgin carbon at this concentration is 0.28 lb/lb. Similarly, Cycle No. 10 on Witco 718 had a feed concentration of ~600 ppm; the equilibrium value is 0.20 lb/lb. Although this comparison shows that Witco 718 achieved a loading closer to equilibrium than Nuchar WV-G, the wide fluctuations in phenol concentration in the feed, evident in Figures 6 and 7, make such a conclusion ill-advised.

From examination of the data in Tables 1 and 2 and from observations during operation of the Demonstration Plant, there does not appear to be any significant difference in the performance of the two carbons tested in the phenol recovery program. The service loading, effluent quality, and regeneration characteristics of the two were essentially equivalent.

The total amount of phenol recovered and recycled from 23 million gallons of brine in 28 cycles of adsorption and regeneration was 116,100 lb. Of this, 112,700 lb was recovered in the 19' high carbon columns in 25 cycles (13 on Nuchar and 12 on Witco). These figures represent an overall average loading in the 19' high columns of 0.167 lb phenol/lb carbon. The overall average feed concentration for the entire demonstration period was 535 ppm. Using the average loading and feed concentration, the average number of gallons processed per cycle in the 19' high columns can be calculated as follows:

$$\frac{0.167\ \text{lb phenol}}{\text{lb carbon}} \times \frac{27,125\ \text{lb}}{\text{column}} \times \frac{1,000,000\ \text{lb brine}}{535\ \text{lb phenol}} \times \frac{1\ \text{gal brine}}{9.15\ \text{lb brine}} =$$

$$928,000\ \text{gal/column cycle}$$

At 60,000 gal of 4% NaOH regenerant, the caustic requirements are 20 lb/1000 gal. This average performance data will be used in determining the cost of treatment in a subsequent section.

Acetic Acid Adsorption and Regeneration

The acetic acid adsorption section of the Demonstration Plant was operated at flow rates of 50-105 gpm (1.0-2.1 gal/min/sq ft) and temperatures of 15° to 70°C. A total of 105 cycles of adsorption and caustic regeneration were carried out on each carbon column. The data on feed brine composition, operating conditions, and product brine quality for cycles 16-100 are summarized in Tables 3 and 4 for Witco 718 and Nuchar WV-G, respectively. Also listed are loadings calculated from the loading curves for some of the cycles.

In the tabulation of feed brine composition, it should be noted that the average phenol concentration in the feed brine began to vary more widely as the operational phase progressed. Similarly, there was a definite decrease in acetic acid concentration in the feed starting around cycle 70. Whereas, 1500-2000 mg/l acetic acid had been the concentration range, it declined to 900-1200 mg/l.

The product brine quality was determined by analyzing 2-hr composite samples of both the effluent from the second or backup acetic acid adsorber when both columns are on line in series flow and the effluent from the one column on line while the other is being regenerated. Therefore, the summary for Witco 718 in Table 3 is the quality of the brine effluent from the Demonstration Plant when that carbon column was backup for the Nuchar WV-G column, or onstream alone. Similarly, the Nuchar WV-G data in Table 4 represent the quality of brine after passing first through the Witco column and then through the Nuchar column or through the Nuchar column alone. These tables are indicative of the product quality of the treated brine produced by the method of operation described earlier.

As reported previously, the phenol content of the effluent brine leaving the phenol adsorbers was in the range 0.5 to 4 mg/l. This phenol is subsequently adsorbed in the acetic acid adsorption columns resulting in a product containing less than 0.1 mg/l phenol. Benzene is strongly adsorbed by carbon and by butyl rubber, so that between the rubber liners on equipment and carbon in the adsorption system, the product contains less than 0.1 mg/l benzene. Acetone is adsorbed at its equilibrium conditions on the carbon in all four adsorbers. The tables reflect an equilibrium amount of acetone passing through the process. There is some disappearance of acetone. We postulate that during regeneration with caustic, some condensation products of acetone (diacetone alcohol and highers) are formed and are permanently held on the carbon and not displaced by the caustic regeneration procedure.

TABLE 3

ACETIC ACID ADSORPTION AND DESORPTION SUMMARY OF CONDITIONS AND PRODUCT QUALITY FOR WITCO 718 CYCLES

FEED ANALYSIS									PRODUCT ANALYSIS							1.
Cycle No.	Flow Rate gpm	ØOH Ads T °C	HOAc Ads T °C	DMK µl/l	Bz µl/l	ØOH mg/l	HOAc mg/l	DMK µl/l	Bz µl/l	ØOH mg/l	HOAc mg/l	Total Carbon mg/l	Unacc Carbon mg/l	% Removal HOAc	HOAc loading lb/lb
17	90	45	42	13	10	500	1500	23	<1	<1	240	166		84.0	
18	80	50	46	40	5		1500	18	<1	<1	60	90		96.0	
19	80	38	34	15	3		1600	23	<1	<1	58	107		96.4	0.056
20	65	45	40	24	4	165	1800	19	<1	<1	23	71		98.7	
24	50	30	24	36	1	175	1700	14	<1	<1	60			96.5	0.056
25	60	40	33	25	10	140	1700	16	<1	<1	90			94.7	0.061
26	90	52	49	20	4	125	1800	19	<1	<1	150			90.6	
27	80	50	47	15	10	250	1700	12	<1	<1	68			96.0	0.045
28	85	52	45	60	15	200	1800	10	<1	<1	220			87.8	
29	75	45	43	50	15	180	1700	9	<1	<1	135			92.0	
30	90	50	47	65	15	125	1400	8	<1	<1	190	108		86.5	0.040
31	90	40	37	62	20	150	1750	8	<1	<1	250			85.7	
32	88	43	40	75	20	-	1500	7	<1	<1	277			81.5	
33	78	42	38	50	10	-	1140	7	<1	<1	150			86.9	
34	80	35	30	35	5	275	1400	4	<1	<1	139			90.0	
35	85	35	30	5	2	240	1350	8	<1	<1	219			83.8	0.046
36	72	28	24	3	1	155	1550	7	<1	<1	284			81.7	
37	80	34	30	24	41	230	1440	13	<1	<1	66	58	25	95.4	
38	78	35	31	3	1	190	1500	7	<1	<1	82	63	27	94.5	
39	62	33	29	12	1	198	1410	20	<1	<1	145	81	13	89.7	
40	70	40	36	2	4	180	1370	17	<1	<1	130	88	27	91.5	
42	70	36	30	0	0	225	1650	7	<1	<1	225	132	28	86.4	0.054
43	55 66 100	44 36 67	30 31 60	0	0	200	1770	14	<1	<1	~100 ~200 ~600				
44	98	67	62	9	5	210	1960	8	<1	<1	853	448	102	56.5	0.022
45	95	66	55	5	1	165	1620	9	<1	<1	383	198	39	76.4	0.020
46	65	32	27	5	1	270	1770	10	<1	<1	211	132	32	88.1	0.043
47	60	25	20	18	1	305	1600	8	<1	<1	127	91	35	92.1	0.043
48	95	50	46	23	1	210	1510	8	<1	<1	258	153	45	82.9	0.046
49	95	50	46	0	0	190	1300	8	<1	<1	292	183	62	77.5	
50	90	44	38	46	2	-	1220	8	<1	<1	90	280			
51	97	50	45	0	0	265	1560	8	<1	<1	273	167	53	82.5	
52	99	77	68	0	0	650	1690	5	<1	<1	505	263	58	70.1	0.026
53	55	58	42	14	8	455	1820	3	<1	<1	95	76	36	94.8	0.042
54	105 80	53 40	52 26	5	1	440	2300	7	<1	<1	245	36	136	89.3	0.055
55	85	45	35	5	1	340	1800	11	<1	<1	59	45	76	96.7	
56	65	30	25	0	0	270	1950	5	<1	<1	145	40	101	92.6	
57	80	38	25	25	0	290	2060	5	<1	<1	72	23	55	96.5	
58	60	30	20	42	0	275	2000	10	<1	<1	176	34	111	91.2	0.055
59	80	45	35	55	0	160	2050	10	<1	<1	433	48	227	78.9	0.042

TABLE 3 (Cont'd.)

FEED ANALYSIS								PRODUCT ANALYSIS							
Cycle No.	Flow Rate gpm	ØOH Ads T °C	HOAc Ads T °C	DMK µl/l	Bz µl/l	ØOH mg/l	HOAc mg/l	DMK µl/l	Bz µl/l	ØOH mg/l	HOAc mg/l	Total Carbon mg/l	Unacc Carbon mg/l	% Removal HOAc	HOAc loading lb/lb
60	90	55	50	60	0	270	1520	11	<1	<1	227	40	182	77.8	0.032
61	90	55	50	66	0	270	1810	15	<1	<1	419	25	202	76.9	
62	75-90	42-48	30-35	120	0	230	1550	12	<1	<1	551	-(15)	212	64.5	
63	90	50	43	65	2	190	1500	14	<1	<1	442	63	248	70.5	
64	90	48	40	102	4	280	1680	8	<1	<1	712	38	328	57.6	
65	95	56	50	70	1	300	1510	8	<1	<1	497	58	261	67.1	0.022
66	85	50	45	70	2	285	1480	9	<1	<1	476	48	244	67/8	0.028
67	95	55	48	70	10	350	1520	7	<1	<1	406	69	235	73.3	0.020
68	98	40	35	60	12	240	1500		<1	<1					
69	92	50	45	60	10	1500	1400		<1	<1	800			43	0.019
*70	92	55	50	7	0	275	1100		<1	<1	600			45	0.019
71	92	55	50	32	0	400	1400		<1	<1	750			47	0.017
72	50	60	53	60	0	NW	1000		<1	<1	250			75	
73	60	65	55	46	9	530	1380		<1	<1					
**74	50		20				1120		<1	<1	200			82	
	23		20				1460		<1	<1	100			93	0.042
75	60	60	50	42	3	400	1300		<1	<1	-300			77	0.034
76	50-60								<1	<1					
77	50-60	40	35	10	0	490	1050		<1	<1					0.030
78	60	50	40	8	0	660	1100		<1	<1	450			59	0.030
79	60	55	45	30	5	620	1100	1	<1	<1					
80	60	62	55	22	13	960	1150	5	<1	<1	490			57	0.021
81	60	55	45	45	6	880	950	3	<1	<1	425			50	0.020
82	60	65	55	60	25	850	1160	3	<1	<1	385			67	0.021
83	60	66	55	75	2	730	1020	1	<1	<1	270			74	0.014
84	60	67	55	70	10	1200	1200	14	<1	<1	610			50	
85	60	62	58	80	10	1000	1200	12	<1	<1	540			55	0.023
86	60	65	62	50	4	800	1400	23	<1	<1	365			74	
67	60	60	56	5	1	500	1200	1	<1	<1	385			68	
89	60	64	60	2	0	200	1000	5	<1	<1	680			32	
90	80	66	64	20	2	300	1100	1	<1	<1	610			44	
91	80	72	68	10	1	300	1000	20	<1	<1	500			50	
92	80	68	64	20	5	400	850	10	<1	<1	520			39	
93	80	68	64	50	10	350	1000	12	<1	<1	500			50	
94	60	64	60	10	1	200	1100	12	<1	<1	360			67	
95	80	72	57	25	2	700	1000	4	<1	<1	500			50	
96	80	66	64	3	0	800	900	7	<1	<1	310			65	
97	80	66	64	40	10	400	950	5	<1	<1	870			9	
98	80	56	54	30	3	500	900	4	<1	<1	370			59	
99	80	60	58	40	5	500	900	7	<1	<1	360			60	
100	80	45	33	60	5	400	900	6	<1	<1	400			55	0.020

*Splitting flow begun

**Recirculating for collection of acetic acid data

TABLE 4

ACETIC ACID ADSORPTION AND DESORPTION
SUMMARY OF CONDITIONS AND PRODUCT QUALITY
FOR NUCHAR WV-G CYCLES

FEED ANALYSIS								PRODUCT ANALYSIS							
Cycle No.	Flow Rate gpm	ØOH Ads T °C	HOAc Ads T °C	DMK µl/l	Bz µl/l	ØOH mg/l	HOAc mg/l	DMK µl/l	Bz µl/l	ØOH mg/l	HOAc mg/l	Total Carbon mg/l	Unacc Carbon mg/l	% Removal HOAc	HOAc loading lb/lb
16	80	37	35	5	1	400	1400	14	<1	<1	90	94		93.5	0.049
17	75	38	35	15	2	340	1500	11	<1	<1	60	110		96.0	
18	85	39	36	40	10	-	1600	13	<1	<1	175	166		89.0	
19	80	42	38	5	1	-	1600	11	<1	<1	95	103		94.1	0.067
23	85	45	40	55	8	320	1700	8	<1	<1	106			93.7	0.029
24	70	40	36	43	10	125	1600	10	<1	<1	115			92.8	
25	70	45	41	10	6	140	1900	10	<1	<1	23			98.8	0.040
26	88	50	47	30	8	150	1600	9	<1	<1	150			90.6	
27	80	50	47	15	10	250	1700	16	<1	<1	46			97.3	0.035
28	85	52	46	60	15	200	1800	14	<1	<1	270			85.0	
29	75	45	42	50	15	180	1700	12	<1	<1	300			82.5	
30	90	50	47	65	15	125	1400	11	<1	<1	340			75.5	0.03
31	80	41	37	55	10	150	1560	15	<1	<1	221	160	(64)	85.8	
32	80	40	36	50	10	-	1340	8	<1	<1	356			73.4	
33	80	25	19	35	5	275	1400	8	<1	<1	277			80.2	
34	82	35	31	7	3	225	1500	8	<1	<1	388			75.1	
35	88	36	31	5	2	215	1500	8	<1	<1	320			78.7	0.041
36	68	30	25	4	2	180	1640	14	<1	<1	285			82.6	
37	80	35	31	6	1	195	1440	18	<1	<1	242			83.2	
38	80	38	35	1	1	190	1500	22	<1	<1	235			84.4	
39	95	48	45	2	1	200	1320	27	<1	<1	382			71.0	
40	65	38	35	13	2	260	1300	31	<1	<1	127	85	(19)	90.2	
41	70	36	30	0	0	225	1650	4	<1	<1	126	91	39	92.4	
42	70/55	45	20	0	0	150	1820	4	<1	<1	443	209	30	75.7	
43	100	70	62	0	0	400	1860	7	<1	<1	258	153	45	86.1	0.026
44	95	66	55	5	0	180	1640	13	<1	<1	1009	560	138	38.5	0.020
45	95	66	55	5	1	270	1680	7	<1	<1	448	260	76	73.3	0.020
46	60	30	26	0	0	375	1560	2	<1	<1	89	99	62	94.3	0.040
47	95	48	43	20	2	350	1520	4	<1	<1	134	86	30	91.2	0.037
48	95	50	46	23	1	210	1510	8	<1	<1	397	214	50	73.7	0.023
49	95	45	38	71	16	315	1330	18	<1	<1	493	275	67	62.9	
50	90	44	38	50	11	-	1340	4	<1	<1	238	121	23	82.2	
51	105	77	68	0	0	650	1690	5	<1	<1	180	111	36	89.3	0.018
52	55	55	42	0	0	345	1780	7	<1	<1	248	137	34	86.1	0.026
53	55	58	42	14	8	455	1820	-	<1	1	-	-		~75	0.026
54	85	40	32	5	3	470	1980	9	<1	<1	314	151	20	84.1	
55	90	45	40	5	1	340	1800	8	<1	<1	183	111	33	89.8	
56	65	30	25	0	0	290	1970	14	<1	<1	212	121	28	89.2	
57	60	30	20	58	0	420	2040	14	<1	<1	262	146	33	87.2	0.038
58	60-85	40	25	40	0	255	2080	9	<1	<1	287	136	15	86.2	0.035

TABLE 4 (Cont'd.)

	FEED ANALYSIS							PRODUCT ANALYSIS							
Cycle No.	Flow Rate gpm	ØOH Ads T °C	HOAc Ads T °C	DMK µl/l	Bz µl/l	ØOH mg/l	HOAc mg/l	DMK µl/l	Bz µl/l	ØOH mg/l	HOAc mg/l	Total Carbon mg/l	Unacc Carbon mg/l	% Removal HOAc	HOAc loading lb/lb
59	80	48	40	58	0	170	2060	16	<1	<1	697	288	0	66.2	0.038
60	90	55	50	66	0	270	1810	16	<1	<1	532	197	(26)	70.6	
61	90	55	50	135	0	270	1750	9	<1	<1	1278	632	116	27.0	
62	75-90	42-48	30-35	120	0	230	1550	9	<1	<1	563	263	32	63.7	
63	90	50	40	45	1	260	1410	12	<1	<1	584	278	27	58.6	
64	90	53	46	45	1	410	1500	8	<1	<1	547	231	8	63.5	0.020
65	90	55	48	70	1	300	1510	8	<1	<1	678	315	39	55.1	0.028
66	90	50	45	70	10	350	1520	12	<1	<1	579	244	5	61.9	0.028
67	95	55	48	33	0	-	1480	7	<1	<1	702	315	30	52.6	
68	100	40	35	85	20	500	1370		<1	<1	600			56	0.031
69	92	50	45	55	20	250	1380		<1	<1					0.026
70	92	55	50	7	0	325	1200		<1	<1					0.020
*71	94-50	55	45	44	0	400	1300		<1	<1	700			46	0.020
72	60	60	50	100	7	635	1250		<1	<1					
**73	50		20				500		<1	<1					
74	60	55	50	100	50	500	1000	3	<1	<1	500			50	0.019
75	60-50		25	20	0	0	1000	1	<1	<1	310			69	0.025
76	60	50	40	5	0	500	1140	1	<1	<1	450			60	0.021
77	60	50	40	25	10	650	1100		<1	<1					0.022
78	60	60	50	5	0	750	1200	1	<1	<1	520			57	0.022
79	60	60	52	35	15	1200	900	9	<1	<1	400			55	0.016
80	60	55	45	32	5	975	1160	1	<1	<1	280			76	0.011
81	60	65	55	7	0	750	1200	7	<1	<1	500			58	0.01
82	60	67	55	100	5	-	1250	3	<1	<1	600			52	0.01
83	60	62	58	80	10	1000	1200	14	<1	<1	430			64	
84	60	65	62	50	4	800	1400	14	<1	<1	500			64	0.021
85	60	60	56	5	1	500	1200	23	<1	<1	630			48	
86	60	60	56	20	2	400	1400	12	<1	<1	790			44	
88	80	66	64	20	2	300	1100	14	<1	<1	590			46	
89	80	72	68	10	1	300	1000	1	<1	<1	190			81	
90	80	68	64	20	5	400	850	3	<1	<1	490			42	
91	80	68	64	50	10	350	1000	7	<1	<1	460			54	
92	60	64	60	10	1	200	1100	5	<1	<1	500			55	
93	80	72	68	25	2	700	1000	12	<1	<1	330			67	
94	80	66	64	3	0	800	900	5	<1	<1	510			43	
95	80	66	64	40	10	400	950	2	<1	<1	180			81	
96	80	56	54	30	3	500	900	0	<1	<1	320			65	
97	80	60	58	40	5	500	900	10	<1	<1	370			59	0.011
98	80	45	43	60	5	400	900	12	<1	<1	230			75	
99	80	62	58	80	5	500	1000	5	<1	<1	550			45	
100	80	60	56	60	2	600	1100	5	<1	<1	290			74	

A calculation of the organic carbon accounted for in the acetone and acetic acid in the product is less than the total organic carbon determined by TOC analysis. This unaccounted for carbon is probably trace amounts of organic or inorganic contaminants other than phenol, benzene, acetone, and acetic acid. The unaccounted for total organic carbon in the product was in the range of 30 to 100 mg/l.

The data in Tables 3 and 4 have been combined with the plotting of breakthrough curves to define the operating and performance limits of the application of activated carbon adsorption to acetic acid and to compare the performance of Witco 718 and Nuchar WV-G in this application. Since a distinguishable difference in the two carbons was obtained, any conclusions as to the operating and performance limits of the system must be prefaced by the comparison of the carbons.

Charts comparing the loading of Witco 718 and Nuchar WV-G as a function of the number of cycles are presented in Figure 9. These graphs do not distinguish any variables in the operation and cover all conditions experienced in the plant. They are an indication of the service life of each carbon. The general trend of the points in both plots is downward, and this reflects both the results of operation at higher temperatures and lower feed concentrations in the later cycles and some not unexpected deterioration in carbon performance. The low loadings seen in these figures are clearly due to temperatures >50°C, since the higher loadings, particularly in the earlier cycles, were obtained at moderate to cool temperatures. In order to get an indication of the capacity of both carbons at lower temperatures after 105 cycles, samples of the carbon in each acetic acid adsorber were withdrawn from a point 4' above the support plate. Batch equilibrium loadings at 25°C and two acetic acid concentrations were measured. The equilibrium loadings after 105 cycles for each carbon were as follows:

Carbon	Equilibrium conc. mg acetic acid/l	Loading lb acetic acid/lb carbon
Witco 718	1270	0.029
	1800	0.040
Nuchar WV-G	1075	0.032
	1700	0.043

These results, when compared with actual loadings obtained in the Demonstration Plant under similar conditions, conform that both carbons, after 105 cycles, have nearly the same capacity that was obtained earlier at moderate to

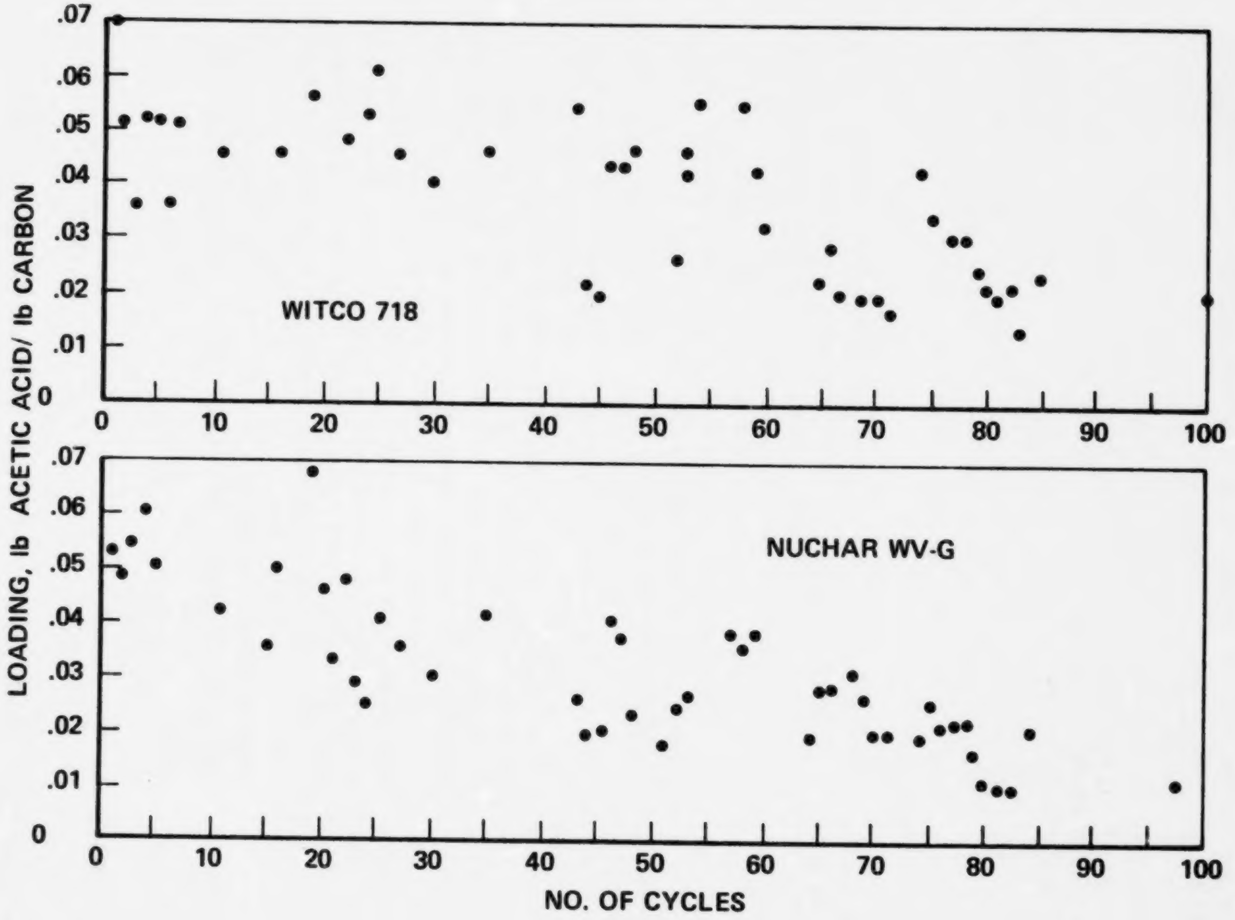


Figure 9

ACTUAL DEMONSTRATION PLANT LOADING OF ACETIC ACID ON WITCO 718 CARBON AND NUCHAR WV-G CARBON AS A FUNCTION OF THE NUMBER OF CYCLES cool temperatures. There has been very little continuing deterioration; the effective loading has stabilized.

Early in the operational period, during the first 10-15 cycles, the performance of the two carbons was similar, generally exhibiting high loadings and good effluent quality (<100 ppm acetic acid). This is shown in Figures 10 and 11, plots of the breakthrough curves of Cycle No. 11 for both carbons at the same conditions. In these and subsequent figures, the alignment of the acetic acid adsorbers is indicated by the notations at the bottom. The Witco 718 column is 501 and the Nuchar WV-G column is 502. In Figure 10, the Witco column 501 is at first on-stream behind the Nuchar column 502, then it is online alone as 502 is regenerated, and then 501 is the lead column when the regenerated 502 is put back on line.

Shortly after Cycle 11, the quality of the effluent from the Nuchar WV-G column began to worsen, as evidenced by levels of acetic acid in the effluent of 200-500 ppm. Plots of breakthrough curves for the two columns at 70 gal/min and 35°C are presented in Figures 12 and 13; the former is Cycle No. 25 for Witco 718; Figure 13 is Cycle No. 22 for Nuchar WV-G. The Witco 718 column continued to produce high quality effluent with good loading, while the Nuchar WV-G removed only 70% of the acetic acid. This trend was observed to continue, and further examples of the differences in the performance of the two carbons at equivalent conditions are presented in Figures 14 and 15, breakthrough curves on Cycle No. 30 for both carbons. It should also be noted that at these more severe conditions, 86 gpm and 45°C, the Witco 718 column is not as effective as previously, but still better than the Nuchar WV-G column.

At 55-57 gal/min and 42°C, the Nuchar WV-G column broke through more quickly and had a much lower loading than the Witco 718. Curves for these conditions are shown in Figures 16 and 17, Cycle No. 53 for Witco 718 and Cycle No. 52 for Nuchar WV-G respectively. A final comparison, obtained when the plant operated at 95-99 gal/min and 70°C, is presented in Figure 18 and again shows Witco 718 to be better. These nine curves (Figures 10-18) were used to illustrate the fact that the Witco 718 column was able to adsorb acetic acid more completely and in higher loading than the Nuchar WV-G column over the range of operating conditions tested. Referring back to Figure 9, the higher loadings achieved with Witco 718 can also be seen. There was no indication from laboratory equilibrium tests that Nuchar WV-G would not perform equal to or better than Witco 718. Laboratory column studies did indicate that Witco 718 gave higher loadings at all temperatures.

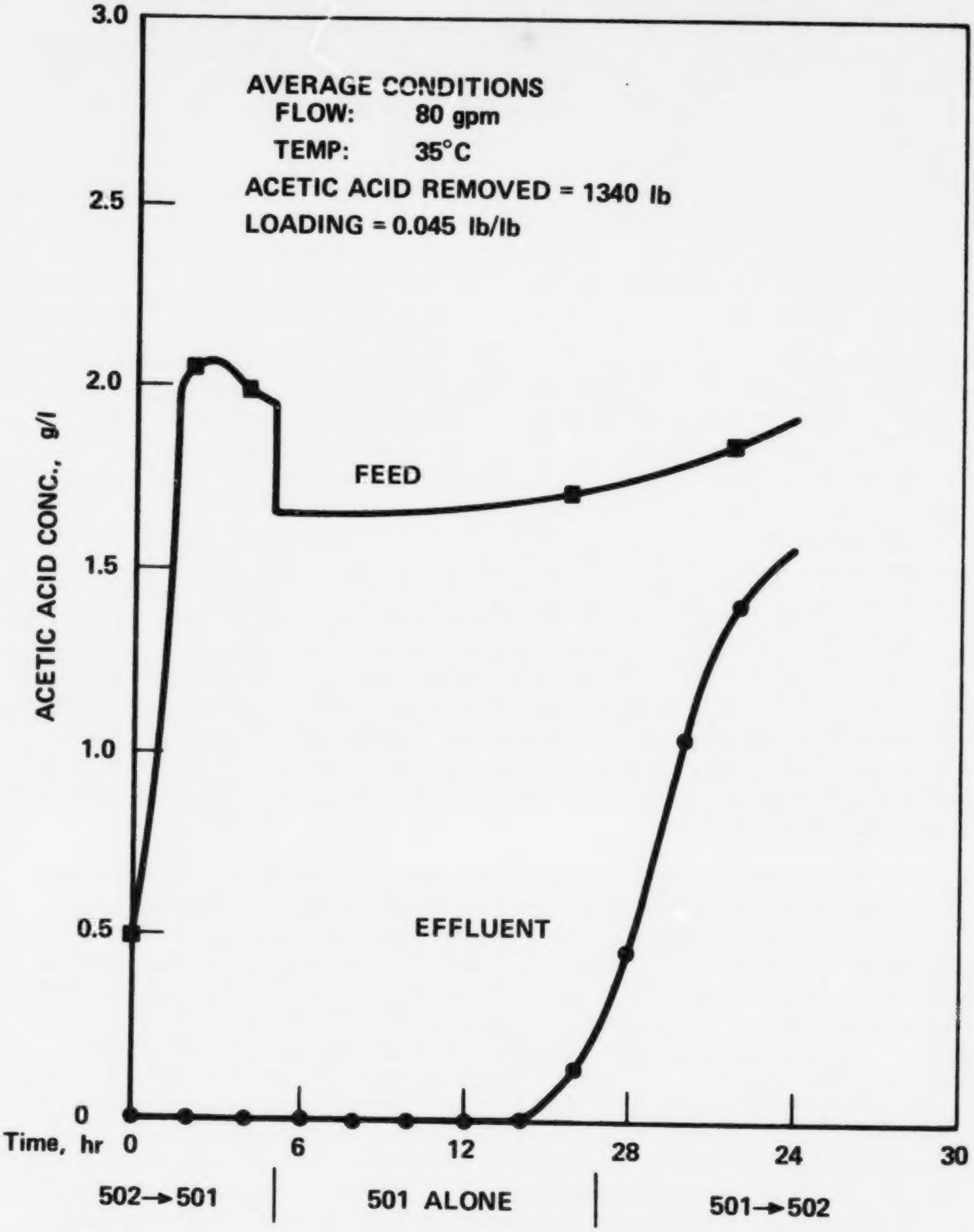


Figure 10

FEED AND EFFLUENT CONCENTRATION CURVE FOR WITCO 718 ACETIC ACID ADSORBER, CYCLE NO. 11

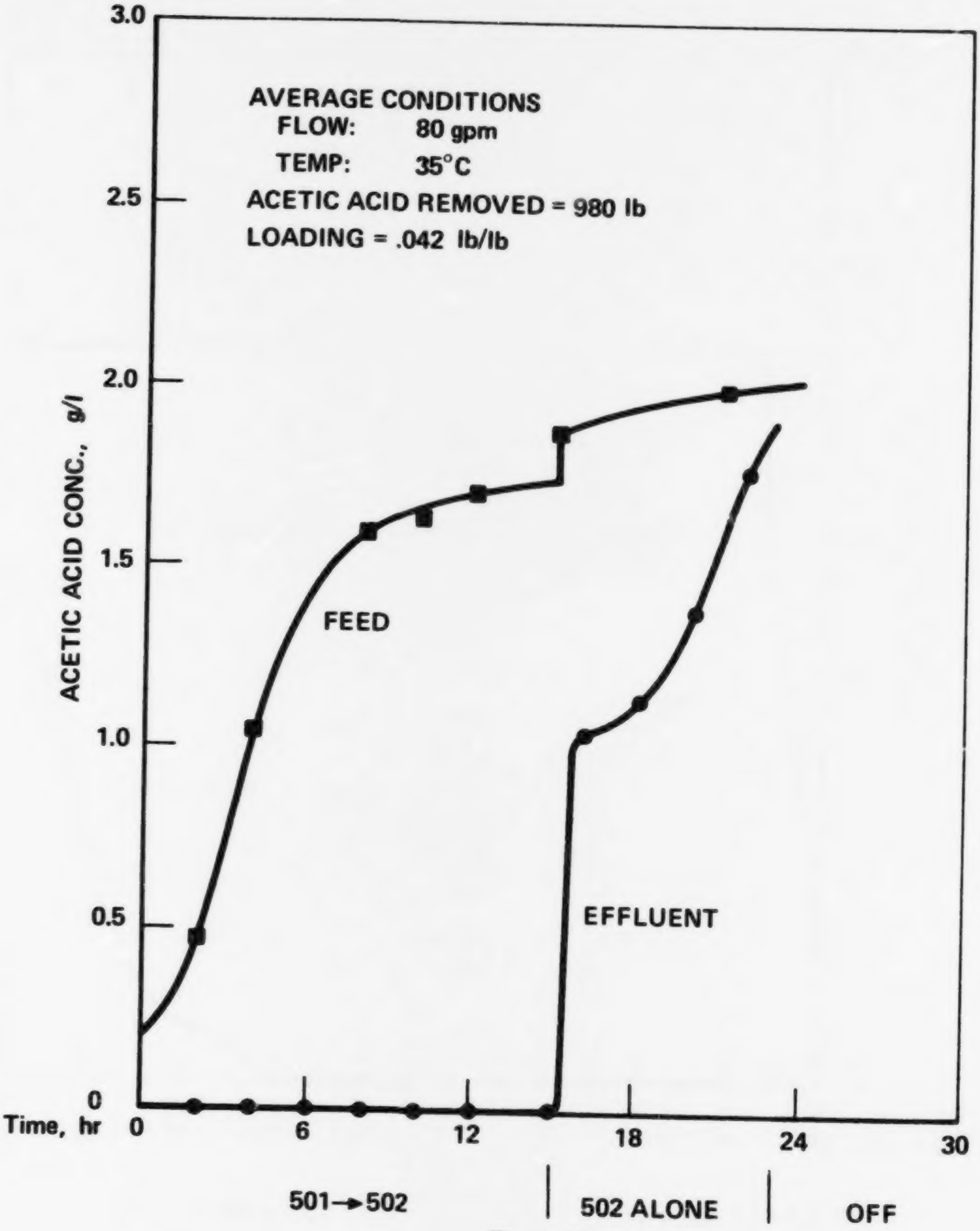


Figure 11

FEED AND EFFLUENT CONCENTRATION CURVE FOR NUCHAR WV-G ACETIC ACID ADSORBER, CYCLE NO. 11

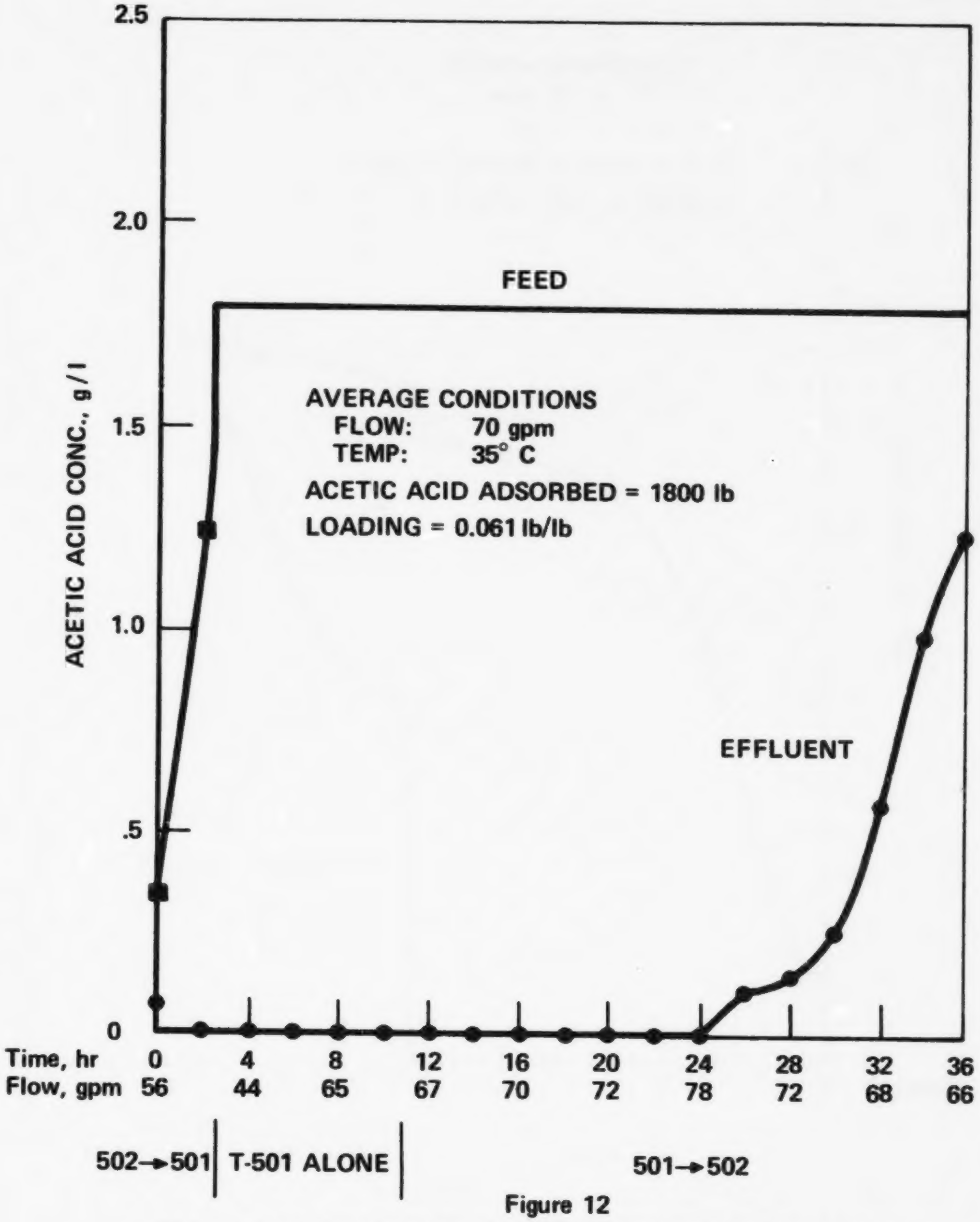


Figure 12

FEED AND EFFLUENT CONCENTRATION CURVE FOR WITCO 718 ACETIC ACID ADSORBER, CYCLE NO. 25

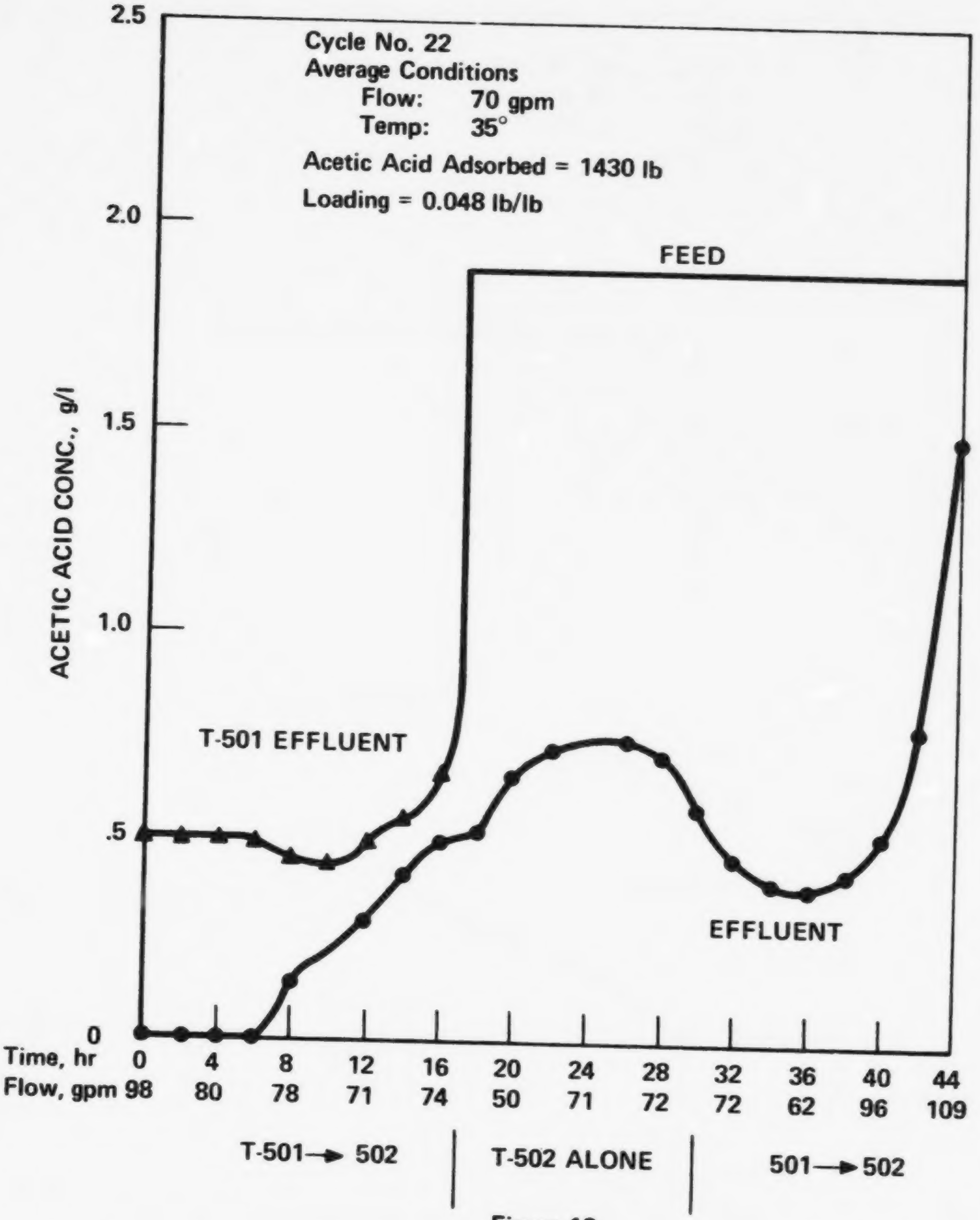


Figure 13

FEED AND EFFLUENT CONCENTRATION CURVE FOR NUCHAR WV-G ACETIC ACID ADSORBER, CYCLE NO. 22

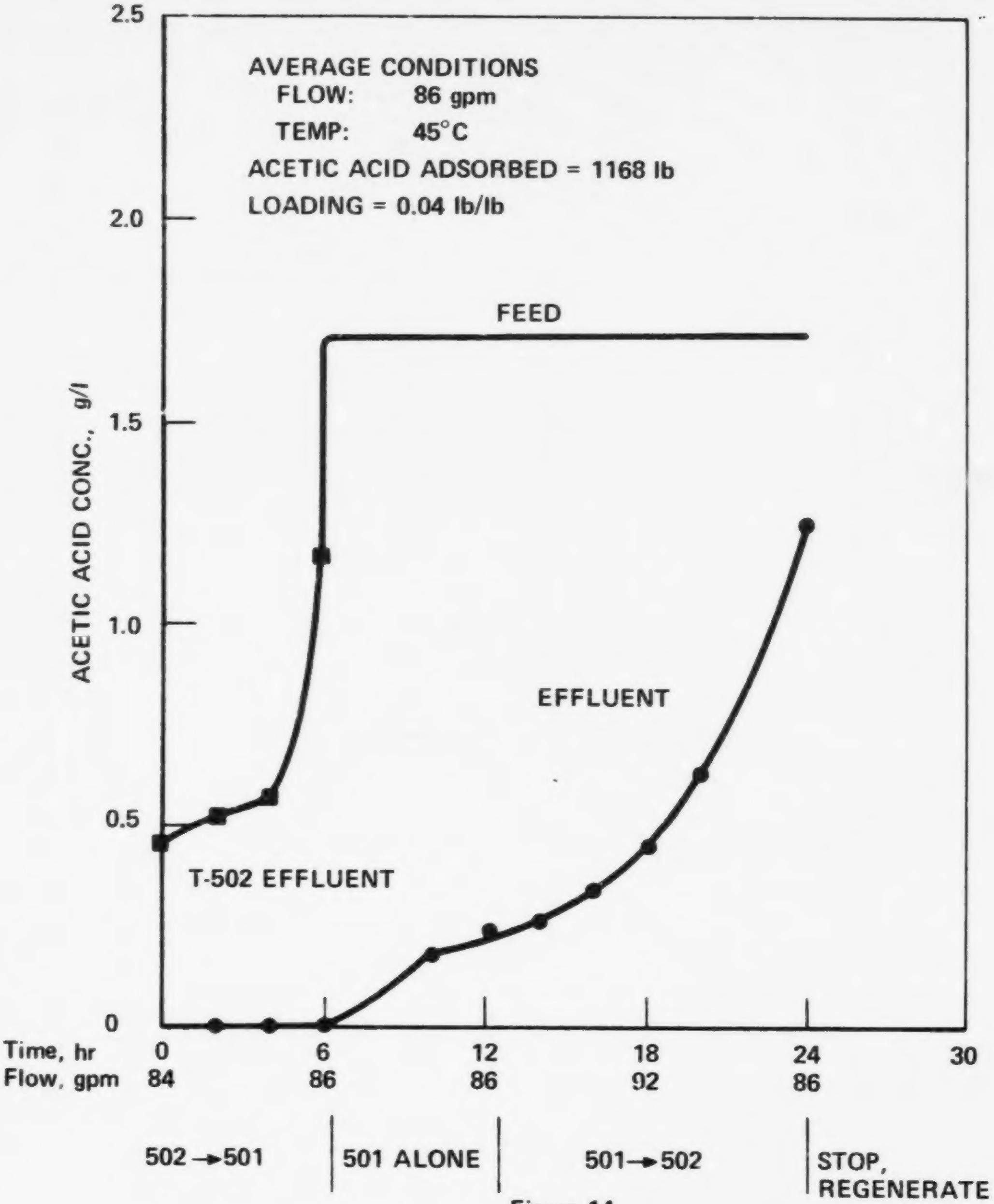


Figure 14

FEED AND EFFLUENT CONCENTRATION CURVE FOR WITCO 718 ACETIC ACID ADSORBER, CYCLE NO. 30

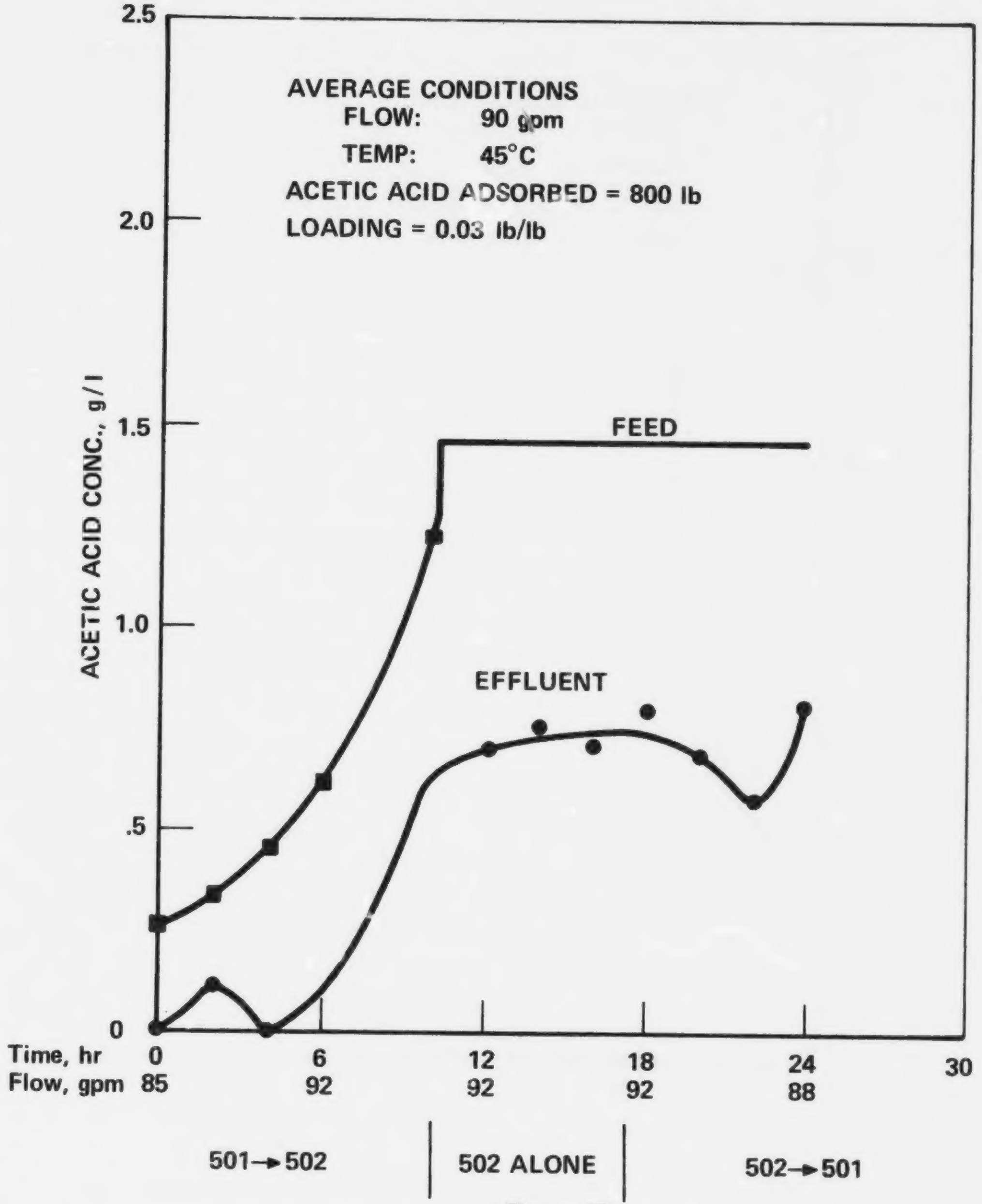


Figure 15

FEED AND EFFLUENT CONCENTRATION CURVE FOR NUCHAR WV-G ACETIC ACID ADSORBER, CYCLE NO. 30

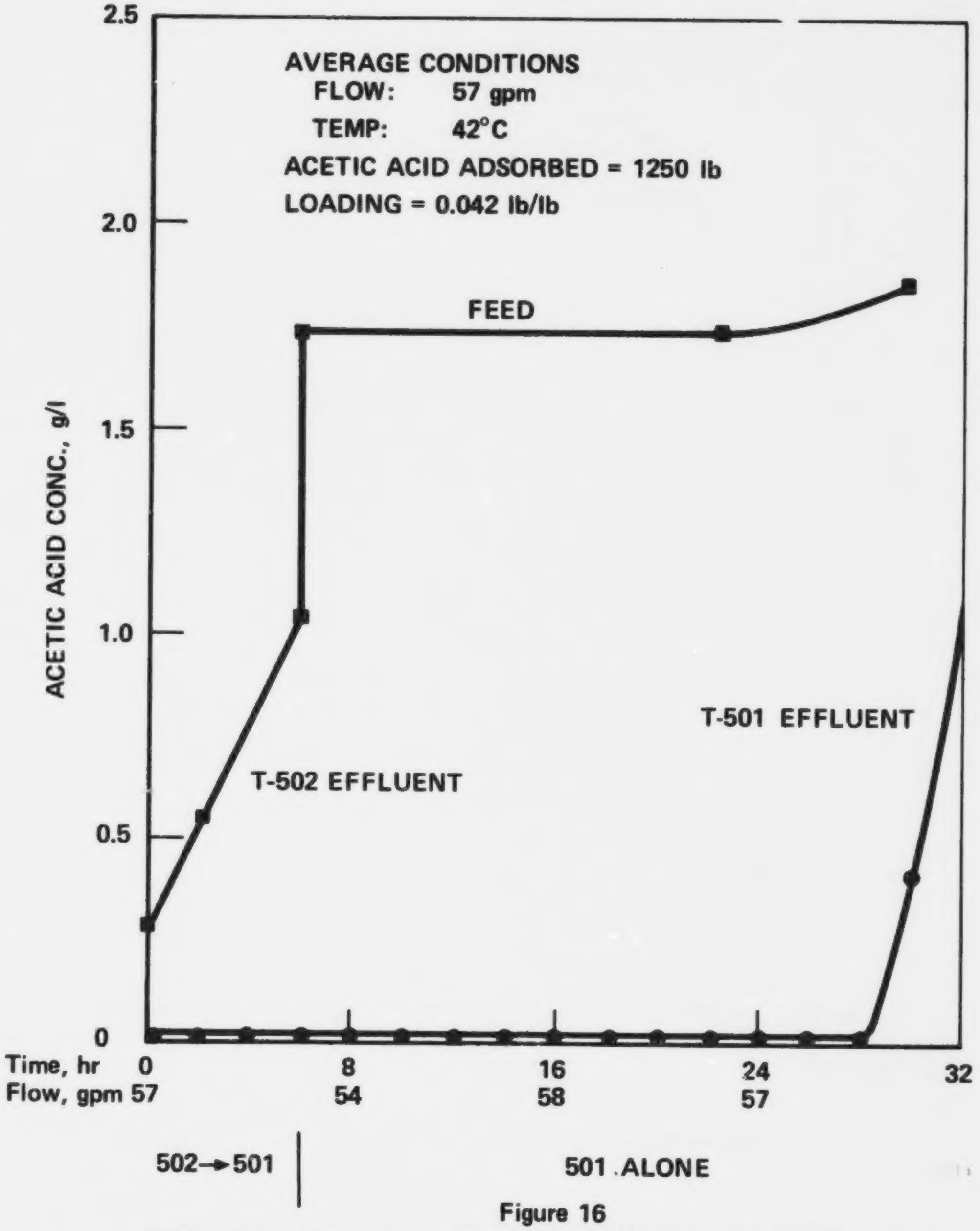


Figure 16

FEED AND EFFLUENT CONCENTRATION CURVE FOR WITCO 718 ACETIC ACID ADSORBER, CYCLE NO. 53

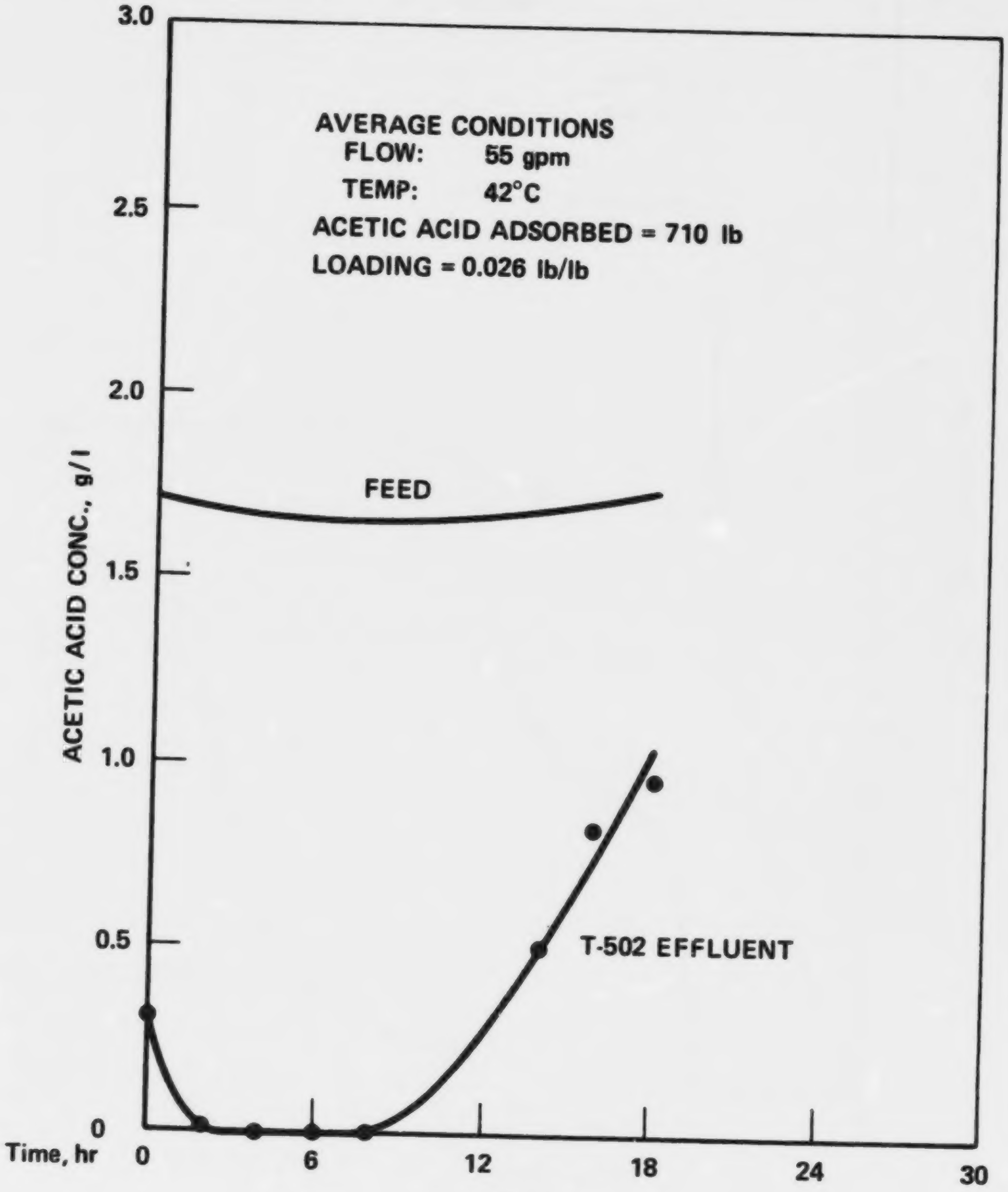


Figure 17
FEED AND EFFLUENT CONCENTRATION CURVE FOR NUCHAR WV-G ACETIC ACID ADSORBER, CYCLE NO. 52

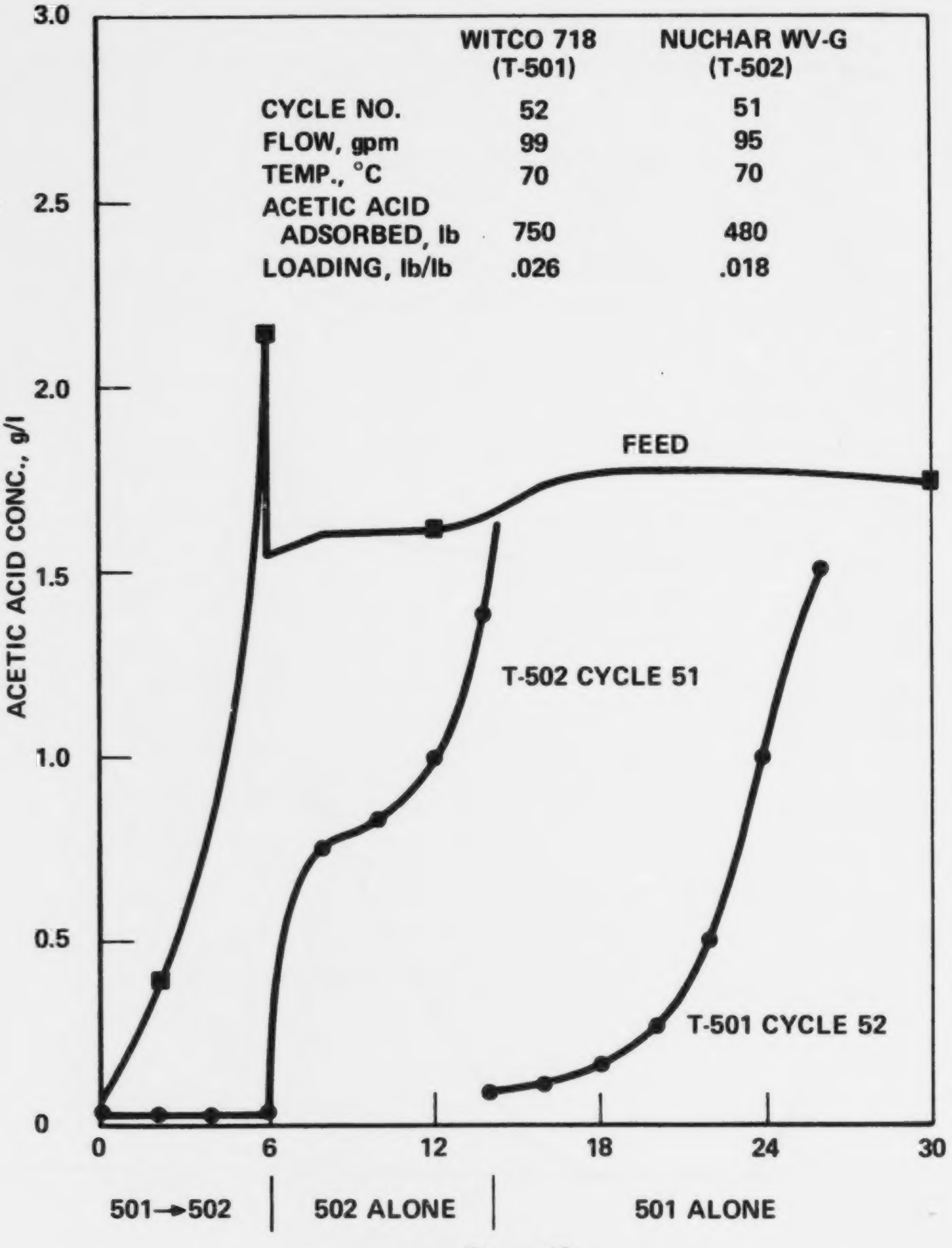


Figure 18

FEED AND EFFLUENT CONCENTRATION CURVES FOR WITCO 718 ACETIC ACID ADSORBER, CYCLE NO. 52, AND NUCHAR WV-G ACETIC ACID ADSORBER, CYCLE NO. 51

Having established the better performance of Witco 718 carbon in acetic acid adsorption, the operating and performance limits for it can now be defined. The capability of the acetic acid adsorption system is best represented by the data collected in the first 6 mos. of the grant during colder weather when cooling of the brine was the maximum. As expected from the laboratory data, the most important variables affecting adsorption of acetic acid were temperature and flow rate. A summary of the operating results on the Witco 718 column is presented in Table 5, showing the effect of temperature and flow rate on acetic acid adsorption. At temperatures greater than 50°C, the loading is too low (0.02-0.03 lb/lb) to be practical. Even at low flow rates of 50-60 gal/min, the low loading produces rapid breakthrough and poor effluent quality. At temperatures of 40-45°C, the loading is high enough and is practical (0.04 lb/lb) and acetic acid levels<100 mg/l can be achieved at flow rates between 50 and 80 gal/min. At temperatures below 40°C, good loading and effluent quality are enhanced. The only significant regime not tested in this grant period was temperatures below 40°C, and flow rates greater than 90 gal/min. It can be concluded that the acetic acid adsorption system can be operated on brine containing 1500-1800 ppm acetic acid at flow rates up to 80 gal/min and temperatures up to 40-45°C; loadings will be ~0.04-0.06 lb acetic acid/lb of carbon, and the effluent will contain less than 200 mg/l of acetic acid, and quite likely less than 100 mg/l, at the less severe conditions. This performance data can be used to calculate some plant capabilities. For a feed brine containing 1500 mg/l acetic acid adsorbed on 8' x 19' carbon column at ≤80 gpm and ≤40°C, a loading of 0.04 lb/lb can be attained and 100,000 gal of brine will be purified to lower than 100 mg/l acetic acid concentrations.

Regeneration of the saturated acetic acid adsorption columns was by desorption with 10% caustic at flow rates of 30 to 60 gal/min. Studies were directed toward minimizing the amount of caustic used and the volume of regenerant. On those cycles when good loadings of acetic acid (0.04-0.06 lb/lb) were achieved, it was necessary to use at least 3600 to 4200 lb of NaOH. When lower loadings (0.02-0.03 lb/lb) were experienced, 2400 lb of NaOH was sufficient to regenerate the column. Curves showing the desorption of acetic acid as sodium acetate and the concentration profile of the caustic in the regenerant are presented in Figures 19 and 20 for the Witco 718 and Nuchar WV-G adsorbers. These are typical of the results obtained when using fresh caustic as the regenerant. The peak acetic acid concentration in the regenerant, expressed in g/l, was 55 to 65. This is the normal range for columns having a high

TABLE 5

SUMMARY OF OPERATING RESULTS FROM ACETIC ACID ADSORPTION ON WITCO 718 SHOWING EFFECT OF TEMPERATURE AND FLOW RATE

Temp, °C	Flow Rate gal/min	Loading lb/lb	Acetic Acid Concentration in Effluent mg/l	Reference Cycle No. in Table 3
>50°	60	0.02	300-600	90-100
	80	0.02	300-600	78-85
	100	0.02-0.026	~500	43,52,65
40-45°	60	0.042	25-100	20,24,53
	80	0.04	60-100	18,27
	80-90		220-280	28,32
	90-100	0.04	150-330	26,30,31,48,51, 63,64
<40°	<80	0.04-0.06	60-225	24,25,33,38,40, 42,46,47
	80	0.045	<100	11

Note: 100 gal/min is equivalent to 2 gal/min/sq ft and a detention time of 60 minutes.

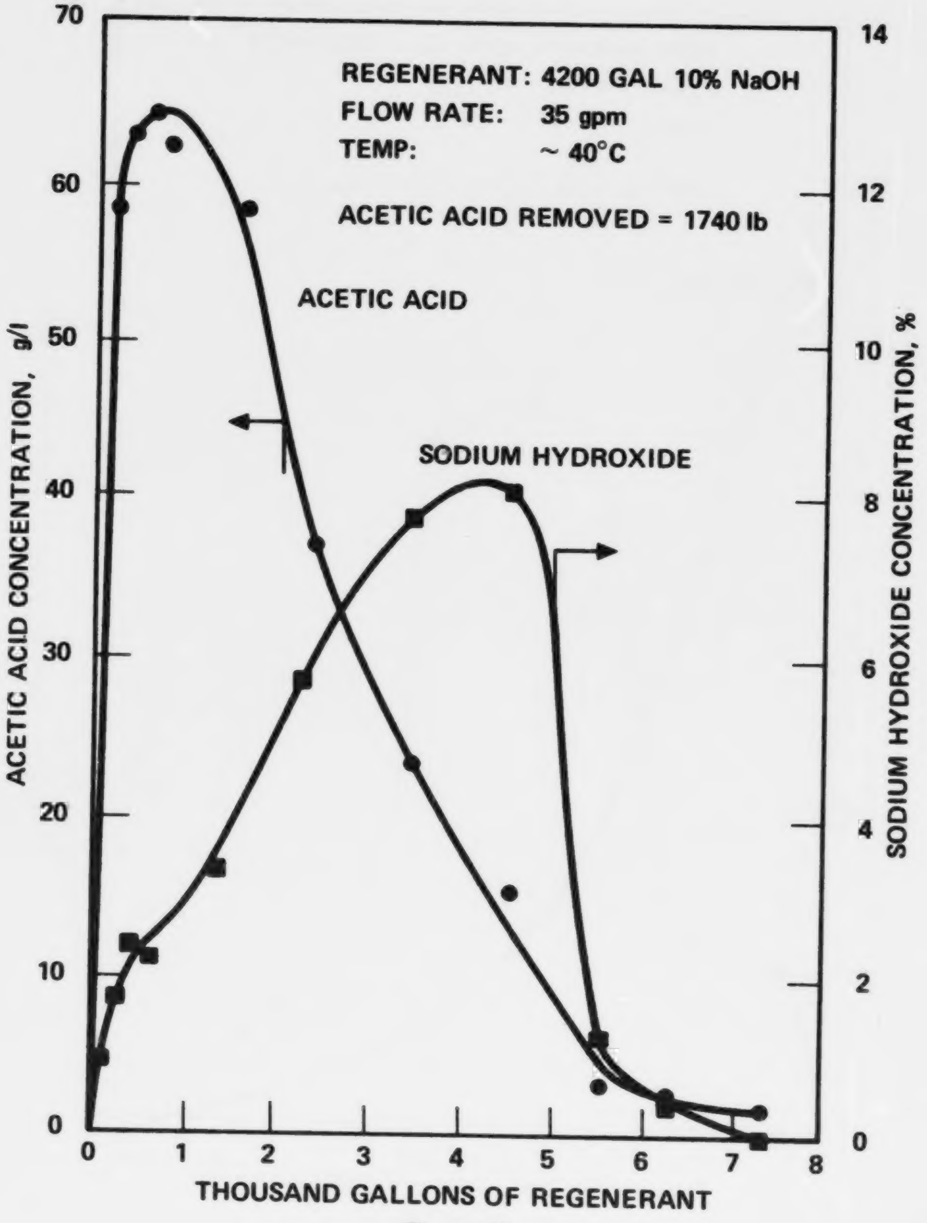


Figure 19

REGENERATION CURVE FOR WITCO 718 ACETIC ACID ADSORBER, CYCLE NO. 22, USING FRESH CAUSTIC

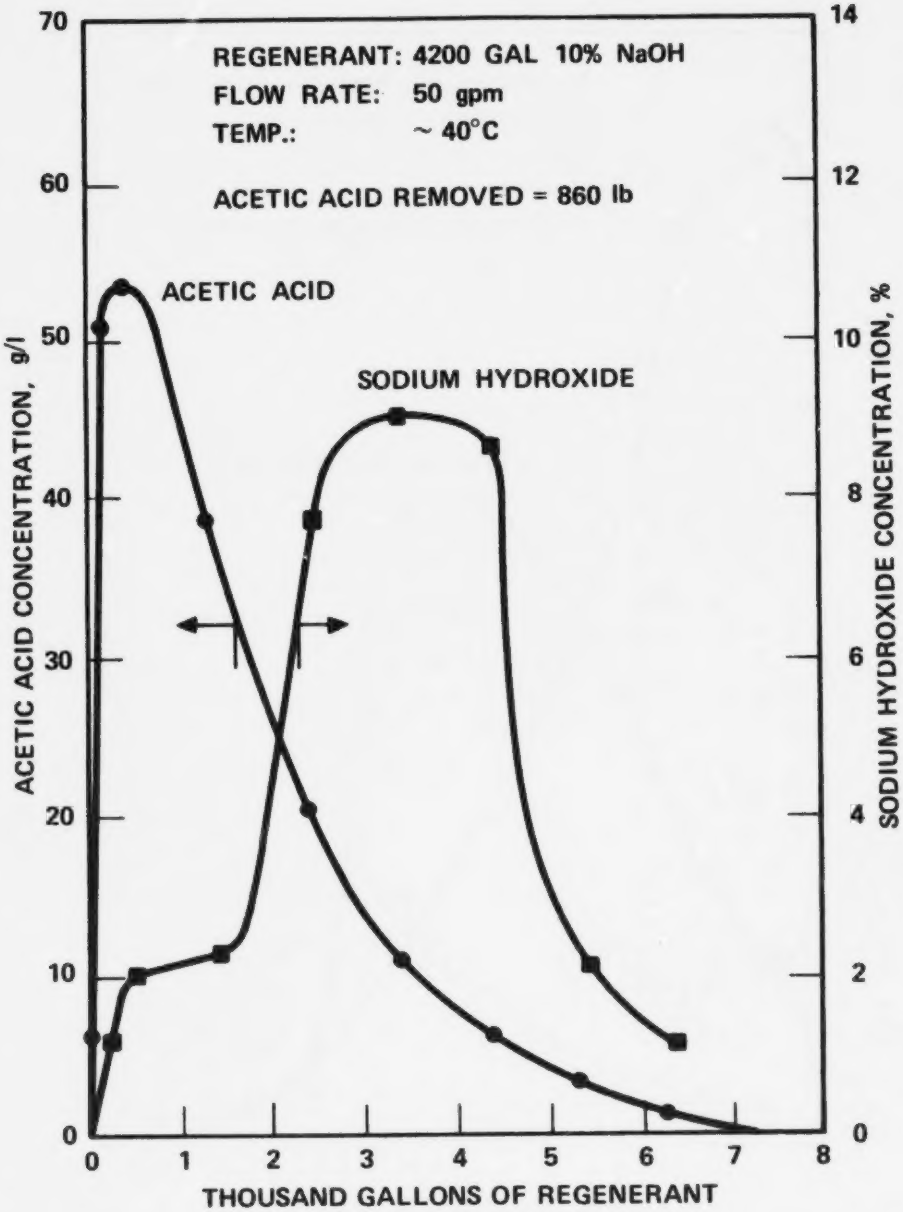


Figure 20

REGENERATION CURVE FOR NUCHAR WV-G ACETIC ACID ADSORBER, CYCLE NO. 21, USING FRESH CAUSTIC acetic acid loading, and it was unaffected by flow rate. When the loading is less, the peak acetic acid concentration is lower. The volume of regenerant was ~6,000 gal. This is a good average number, and it is not changed appreciably when 2400 lb NaOH are used on low loading cycles. The sodium hydroxide content in the regenerant, as anticipated, was essentially a mirror image of the acetic acid concentration.

The presence of the unused caustic in the tail of the regenerant led to the studies on saving the last few thousand gallons of regenerant, fortifying it with strong caustic to 10%, and reusing it as regenerant on the subsequent cycle. Typical regeneration curves resulting from this method of operation are shown in Figure 21. The curves are somewhat flatter than those in Figures 19 and 20 even though there was not much difference in the amount of acetic acid desorbed. Several combinations of regenerant saved and the amount of strong caustic used to fortify it were tested. The total amount of caustic regenerant fed to the column was varied from 2300 gal to 4500 with no appreciable effect on the net volume of regenerant for disposal. It was typically 3500-4000 gallons. Thus, it was possible to reduce the amount of regenerant from each cycle to 0.5-0.6 bed volumes or 4-4.5% of the feed volume.

Recycle of weak regenerant has one drawback - the level of acetic acid in the weak regenerant can begin to build up and make the regeneration less efficient. This is best handled by periodically using fresh regenerant for a few cycles.

The amount of caustic soda used per cycle is not affected by recycle of regenerant. The optimum for a column having a high loading of acetic acid was ~3600 lb NaOH. This represents a caustic requirement for regeneration of 36 lb NaOH/1000 gal. The amount of HCl used per cycle was 8 lb/1000 gal for pH adjustment and 6 lb HCl/1000 gal for regeneration.

Evaluation of Materials of Construction

In one year of operation, the following failures in equipment were experienced:

1) Ductile cast iron pump in 100°C, 18% NaCl, pH 7-9 service failed in three months by erosive and corrosive attack. It was replaced with a cast 316 stainless steel pump and very low erosive or corrosive wear were experienced in the next nine months.

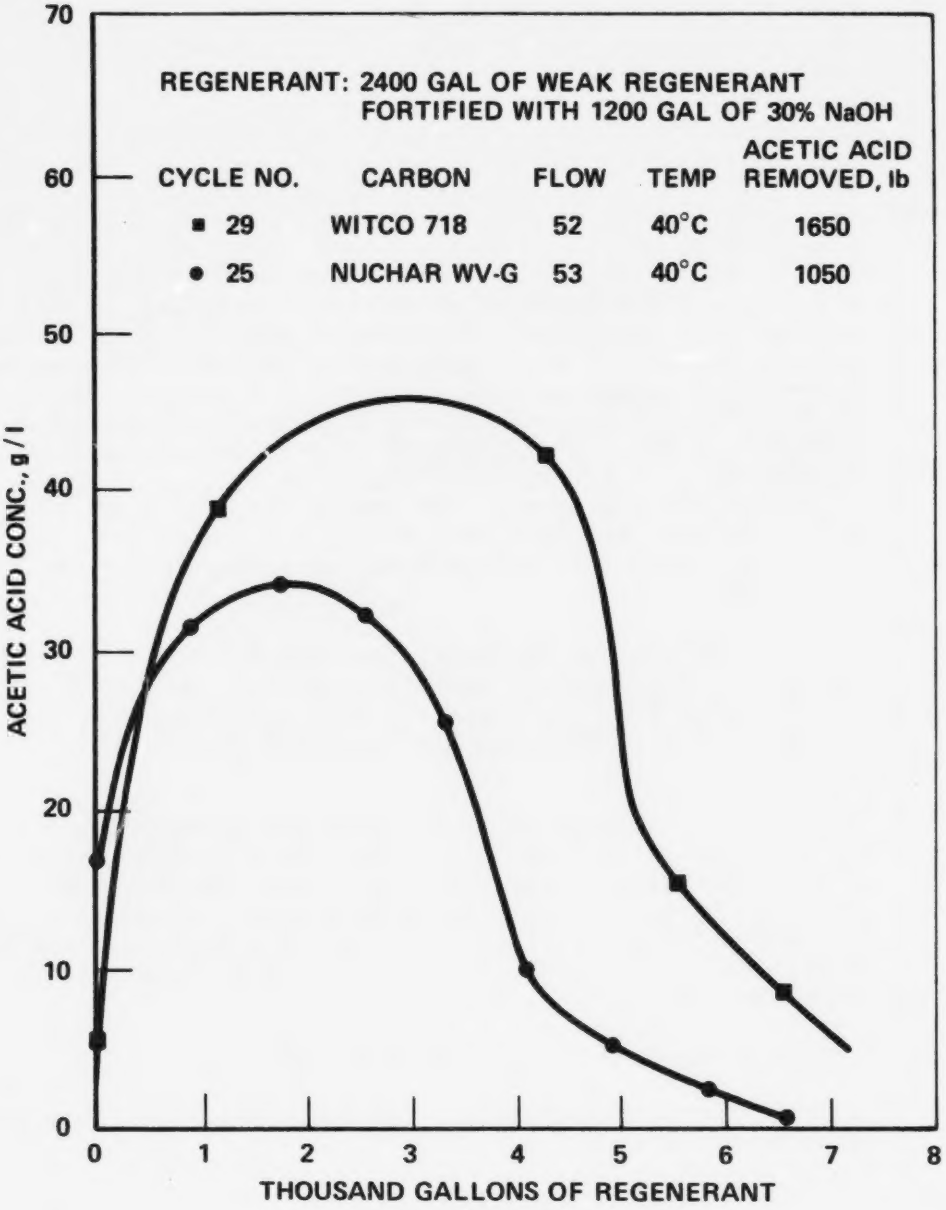


Figure 21

REGENERATION CURVES FOR ACETIC ACID ADSORBERS USING RECYCLE OF FORTIFIED WEAK REGENERANT

2) Ductile cast iron pump in 60°C, 18% NaCl, pH 6-9 service failed in 11 months by erosive and corrosive attack. It was replaced with a cast 316 stainless steel pump.

3) The rubber-lined agitator in acid brine service (pH 2-3) failed because a pinhole developed, caused by flexing of the agitator shaft. The steel was then attacked and one blade fell off in 10 months service. A replacement rubber-lined agitator failed by the same mechanism in 6 weeks. Rubber lining is unsuitable for agitator blade service although it is satisfactory for tank linings. A replacement, all-titanium agitator was ordered and installed. In the interim, the tank was agitated by recirculating its contents using a polypropylene-lined centrifugal pump.

4) Chlorinated organics periodically present in the crude HCl caused failure in polypropylene-lined pipe. This pipe was replaced with FEP polymer lining.

5) Although the air cooled heat exchanger did not suffer corrosive failure, finely divided inorganic sludge that did not settle in the clarifier plugged the passages and increased pressure drop and decreased heat transfer efficiency. This problem was corrected by a standard acidizing treatment.

Corrosion test coupons installed in a 4" pipeline containing 100°C salt brine at pH 7-9 gave a corrosion rate of 0.007 inches/year. Therefore steel is a suitable material for pipelines with moderate velocites. However, centrifugal pumps which operate at high velocity are subject to a combined erosive and corrosive attack and fail in the same service. At the corrosion rates experienced, we would project a service life in excess of 10 years for the major equipment installed in the plant.

Costs

Capital

The total installed capital cost for this 100 gal/min Demonstration Plant was $592,000. This was broken down as follows:

Major equipment purchases	$138,100
Installation of equipment	273,700
Instrumentation	72,000
Engineering	75,000
Carbon, initial charge	33,200
	$592,000

Approximately one-half of this cost can be allocated to the phenol adsorption system and one-half to the acetic acid adsorption system. An additional $44,200 was spent in constructing and installation of the chlorine test cells.

Operating

The significant items affecting the operating costs for this adsorption system are carbon life (or carbon makeup requirements), chemicals for pH changes and regeneration, labor, maintenance, utilities, and depreciation. Carbon life has a linear effect on carbon makeup costs and is important to the economics of wastewater purification by activated carbon with caustic regeneration.

Phenol Plant Brine Purification

The Demonstration Plant does not have adequate cooling to operate at 100 gal/min capacity. A feed brine cooler exchanging heat between the cool product brine and the hot feed brine would be a required additional capital expense to assist the air cooler particularly in the summer. Also, it would be desirable to add instrumentation to automate the system to eliminate the need for full-time operators. We project that labor needs could be met with incremental labor. The additional capital required is estimated to be $100,000, bringing the total to $692,000.

With these modifications, the cost of purifying 100 gal/min of Phenol Plant brine by a two-stage carbon adsorption process can be projected.

$$\text{Plant capacity} = \frac{100\text{ gal}}{\text{min}} \times \frac{1440\text{ min}}{\text{day}} \times \frac{365\text{ days}}{\text{yr}} \times \begin{array}{c}0.90\text{ operating}\\ \text{factor}\end{array}$$

$$= 47{,}500{,}000\text{ gal/yr}$$

From previously derived figures for the volume of brine processed per cycle (928,000 gal for phenol and 100,000 gal for acetic acid) the annual number of cycles required for each of the phenol and each of the acetic acid adsorbers processing 47.5$\overline{\text{M}}$ gal of brine is 25 and 237.

The Demonstration Plant operated through 14 cycles on phenol and 105 cycles on acetic acid and was still effective. It is reasonable to assume that the effective carbon life for the optimized process would be one year. For the phenol columns, the carbon life can quite likely be even longer. Since each carbon column contains $8300 worth of carbon, the carbon makeup cost if replaced after one year would be $0.35/M gal for phenol and $0.35/M gal for acetic acid adsorption.

The projected chemical costs for the optimized two-stage adsorption system are:

NaOH for phenol regeneration	:	20 lb/M gal @ $70/ton=$0.70/M gal
for acetic acid regeneration	:	36 lb/M gal @ $70/ton=$1.26/M gal
HCl for process	:	14 lb/M gal @ $30/ton=$0.21/M gal
		$2.17/M gal

By recycle to the Phenol Plant, the sodium phenate and the caustic used for phenol regeneration are recovered. The recovery value of the phenol is $0.35/M gal and caustic is $0.70/M gal; therefore, the recycle of the phenol regenerant reduces net raw material costs by $1.05M/gal.

Actual maintenance and utilities costs were measured over six months of routine operation, and the annual maintenance costs (materials and labor) were projected to be $25,000. The annual utilities costs were projected to be $8600.

The operating costs are tabulated in Table 6 per 1000 gal of brine purified.

TABLE 6

PROJECTED COSTS FOR PURIFICATION OF 100 GAL/MIN OF PHENOL PLANT WASTE BRINE

	$/1000 gal
Depreciation @ $69,200/yr (10 yr straight line)	1.45
Maintenance @ $25,000/yr	0.52
Utilities @ $8600/yr	0.18
Chemicals	2.17
Labor(incremental with automation)	0
Carbon Makeup	0.70
Total Projected Costs	$5.02/M gal
Credits	
Recovery of phenate regenerant	1.05/M gal
Salt recycle	1.00/M gal
Reduction in brine disposal cost	1.65/M gal
Total Credits	$3.70/M gal
Net Operating Cost	$1.32/M gal

The major cost items are seen to be depreciation, the caustic soda required for acetic acid regeneration, and carbon.

The above cost data can be manipulated to develop treatment costs for separate removal of phenol and acetic acid. By assigning one-half of the capital to the phenol adsorption system and one-half to the acetic acid adsorption system, the operating cost per lb of phenol recovered develops as follows:

Basis: Recovery of 212,000 lb phenol/yr from 100 gal/min waste containing 535 ppm

	$/lb phenol
Depreciation @ 10 yr straight line $692,000 ÷ 2 x 1/10=$34,600/yr	$0.163
Maintenance, $12,000/yr	0.056
Utilities, $4,300/yr	0.020
Chemicals, no cost if recovered	0
Labor	0
Carbon Makeup @ $0.35/M gal	0.078
Recovery cost/lb phenol	$0.317

Similarly, the unit cost for removing acetic acid from a wastewater by carbon adsorption can be calculated:

Basis: Removal of 90% of the acetic acid in 100 gal/min waste containing 1500 mg/l, or 535,000 lb/yr.

	$/lb acetic acid
Depreciation, $34,600/yr	$0.065
Maintenance, $12,000/yr	0.022
Utilities, $4,300/yr	0.008
Chemicals, $1.47/M gal	0.125
Labor	0
Carbon Makeup @ $0.35/M gal	0.031
Treatment cost/lb acetic acid	$0.251

SECTION VII

CHLORINE TEST CELLS

Construction

The two 2660 ampere chlorine cells for testing phenate brine were built using standard cathode pockets and graphite anodes. Scaling down of the cells to test-size was accomplished by reducing the number of pockets and anodes. The cells were set up at the Chlorine Production Plant. D.C. power was supplied by a Udylite model 4ADW-5M012-101 constant current rectifier. Each cell had a saturator in the feed brine system.

Feed brine for Cell 1 operating on pure brine was made by dissolving salt in steam condensate and required no treating. Cell 2 which operated on purified phenate brine had a 200 cu ft batch settling tank for the removal of calcium, magnesium and iron impurities, and a storage tank for finished brine.

Additional equipment associated with the cells included automatic head controls with a brine pump and a heater for each cell and a Beckman 315A infrared continuous CO_2 analyzer for the chlorine.

Operation

The two cells were started up September 1, 1970, using regular chlorine plant feed brine. After a three-week checkout period to make sure the cells were operating normally, feed streams to the cells were switched to the test brines.

Cell 1 - Pure brine made from salt and condensate to serve as a reference.
Cell 2 - Phenate brine purified in the Demonstration Plant.

The cells were switched to regular chlorine plant feed brine for three weeks in January and again in June to check for permanent changes caused by the test brine.

Results

Based on six ampere laboratory cell test results as well as plant experience attempting to run unpurified phenate brine through production cells, the most likely problem areas were defined as follows:

1. Brine treating
2. Diaphragm plugging
3. Loss of current efficiency
4. Voltage
5. Graphite wear
6. Product quality

Analyses of the test brines, chlorine and caustic as well as other pertinent cell variables averaged over the entire test period are given in Table 7. These data are based on feeding undiluted phenate brine, so that any dilution of the phenate brine with brine from other sources would produce a corresponding reduction in the effects on cell operation.

The most likely problems listed above are discussed in the following paragraphs. These were the only areas where the purified phenol brine was observed to have any effect on cell operation.

1. Brine treating

   The feed brine analyses in Table 7 indicate that there was some difficulty in treating the iron out of the phenate brine. The high iron resulted from the tendency of organics to complex iron and reduce settling rates. The problem is less with purified phenate brine than with raw phenate brine, and the brine plant has the capability to produce brine with less than 1 ppm iron when purified phenate brine is recycled. No difficulty was experienced in removing either calcium or magnesium.

2. Diaphragm Plugging

   The slightly higher head and caustic strength of Cell 2 indicate some diaphragm plugging. This amount of plugging is normal for brine which contains high iron. There is no evidence that the organics in the phenate brine directly plugged the diaphragm. When the cells were switched from the test brines to regular plant feed brine there were no sudden changes in caustic strength or voltage.

3. Loss of Current Efficiency

   The current efficiency of the two cells was identical, and the current efficiency loss associated with raw phenate brine in earlier tests was com-

TABLE 7

AVERAGE ELECTROLYTIC TEST CELL OPERATING DATA

	Cell 1	Cell 2
Type feed brine	Pure brine	Purified phenate brine
Brine Analyses		
NaCl g/l	311	310
$SO_4^{=}$ g/l	0.83	1.6
Ca^{++} ppm	1.7	2.5
Mg^{++} ppm	0.2	0.2
Fe^{++} ppm	0.3	1.4
Organic Carbon ppm	16	280
Inorganic Carbon ppm	14	47
Sodium Acetate ppm	<5	553
Phenol ppm	0	4
Acetone ppm	<2	8
Days Operated	206	210
Volts	3.01	3.11
Current, amperes	2660	2660
Temp. °C	69	70
Head, inches	6.5	8
Chlorine Current Efficiency	97.90	97.81
Cl_2 Analyses (air free)		
$\%Cl_2$	97.87	98.49
$\%CO_2$	0.49	0.85
$\%O_2$	0.60	0.32
$\%H_2$	1.04	0.38
$\%COCl_2$	nil	0.001
Caustic Analyses		
NaOH g/l	97	102
NaCl g/l	197	191
$NaClO_3$ g/l	0.084	0.107
Organic Carbon ppm	29	223
Sodium Acetate ppm	18	480
Phenol ppm	1.4	1.9
Acetone	<2	<2

pletely eliminated. Experience with raw phenate brine recycle to chlorine cells showed that oxidation of phenol and acetone in the feed brine produce most of the efficiency loss. These compounds - particularly phenol - are very effectively removed in the Demonstration Plant.

4. Voltage

The higher voltage of Cell 2 was associated with difficulty in removing the iron in brine treating and subsequent plugging of the diaphragm. Dilution of the brine in plant operation improves the brine treating and reduces the tendency for the voltage to increase.

5. Graphite Wear

There was no significant difference in graphite wear between the cells. The slightly higher CO_2 content of the chlorine with purified phenate brine (which normally is formed from the graphite and indicates graphite wear) resulted from the oxidation of organics in the feed brine. The extent to which this takes place is measured by the difference in organic content of the feed brine and the cell effluent.

6. Product Quality

Infrared analyses of the chlorine for organics showed similar spectrum for the cells operating on pure brine and purified phenate brine. Chlorinated aromatics, which would cause a great deal of trouble in the chlorine compression equipment were not present in the chlorine. Although a small quantity of phosgene is produced with purified phenate brine, the amount will not be a problem.

The organic contamination of the caustic is largely a problem of meeting the specifications of the product for sale. Samples of the cell effluent produced no unusual foaming problems when evaporated to 50%. The caustic from Cell 1 which operated on pure brine contained 29 ppm organic carbon, up slightly from the 16 ppm in the feed brine. Oxidation of the graphite anode is the source of the additional organic carbon. The organic carbon in the caustic from Cell 2 comes primarily from the feed brine. Much of this organic carbon is in the form of sodium acetate. About 90% of the sodium acetate in the feed brine enters into no reaction in the cell and ends up as a contaminant in the caustic.

The sodium acetate content of the purified phenate brine fed to Cell 2 varied from 77 to 1000 ppm during the run, depending on the flow rates and conditions of the towers at the Demonstration Plant. The high acetate level seemed to have no harmful effect on cell operation other than contamination of the caustic soda effluent.

Conclusions

Waste phenate brine can be used as chlorine cell feed without severe operating penalties if it is purified equivalent to that treated in the Demonstration Plant.

Problems that were experienced when raw phenate brine was used, but are eliminated with the purified brine are:

1. Current efficiency loss.
2. Organic contaminants in the chlorine causing plugging of compression equipment.

Problems that are reduced but not completely eliminated by purification in the Demonstration Plant are:

1. Interference of organics with brine treating (particularly iron).
2. Organic contamination of caustic.

SECTION VIII

LABORATORY STUDIES

Phenol Adsorption and Regeneration

Batch equilibrium studies were conducted to provide guidance for the selection of the type of carbon and for the operational phase of the Demonstration Plant as to the effects of certain critical variables. Carbon from 8 manufacturers, and a total of 12 types were initially screened for phenol capacity with the results shown in Figure 22. Most of the carbons were equivalent in these virgin carbon tests. Because of its superior performance for acetic acid adsorption, Witco 517 was selected for further studies. Phenol adsorption and desorption kinetics were measured, and 90% equilibrium was reached in 1 hour regardless of particle size. Rates at 60°C were equivalent to rates at 25°C. The effect of pH on phenol loading was examined over the range of 0.5 to 12.0. The results in Figure 23 shows a maximum loading in the pH range 6.0 to 8.5 at 25°C. Next, the effect of caustic strength on phenol loading was tested on virgin Witco 517. The optimum caustic soda strength at 25° and 60°C for desorption was determined to be around 4% as seen in Figure 24. This batch equilibrium test was conducted by shaking a fixed initial concentration with the same amount of carbon in various caustic soda concentrations. Thus, the equilibrium concentration of phenol varied. When this effect was recently checked again, keeping the equilibrium phenol concentration constant, the optimum caustic strength was less pronounced as shown in Figure 25. The optimum range has broadened to at least 2 to 8% NaOH at phenol concentrations of 400 and 1600 mg/l.

With the selection of Witco 718 and Nuchar WV-G activated carbons as those to be loaded into the Demonstration Plant columns, and the subsequent discovery of the need to acid-wash the acid soluble compounds from the carbon, phenol adsorption and desorption isotherms at various temperatures were determined. The isotherms for phenol adsorption on acid-washed Witco 718 in 20% brine at pH 7 at 25°, 40°, and 60°C are presented in Figure 26. The 40° and 60°C lines coincide for all practical purposes. Similar isotherms at 25° and 60°C for acid-washed Nuchar WV-G are shown in Figure 27. Noteworthy is the observed crossing of the two lines.

The isotherms for sodium phenate adsorption (phenol desorption) on acid-washed Witco 718 and Nuchar WV-G are presented in Figures 28 and 29 respectively. Temperature

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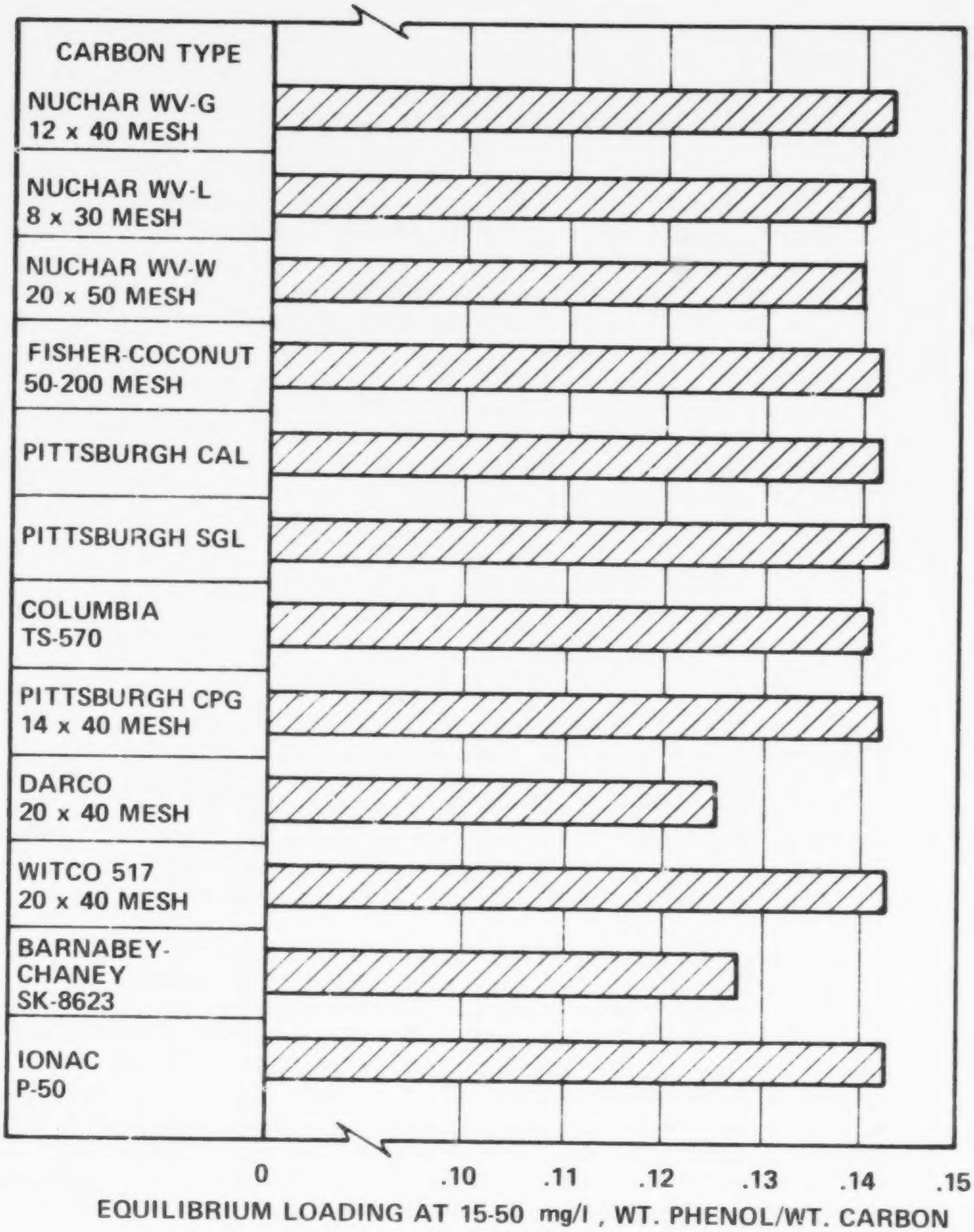


Figure 22

EQUILIBRIUM PHENOL LOADING FOR VARIOUS VIRGIN ACTIVATED CARBONS

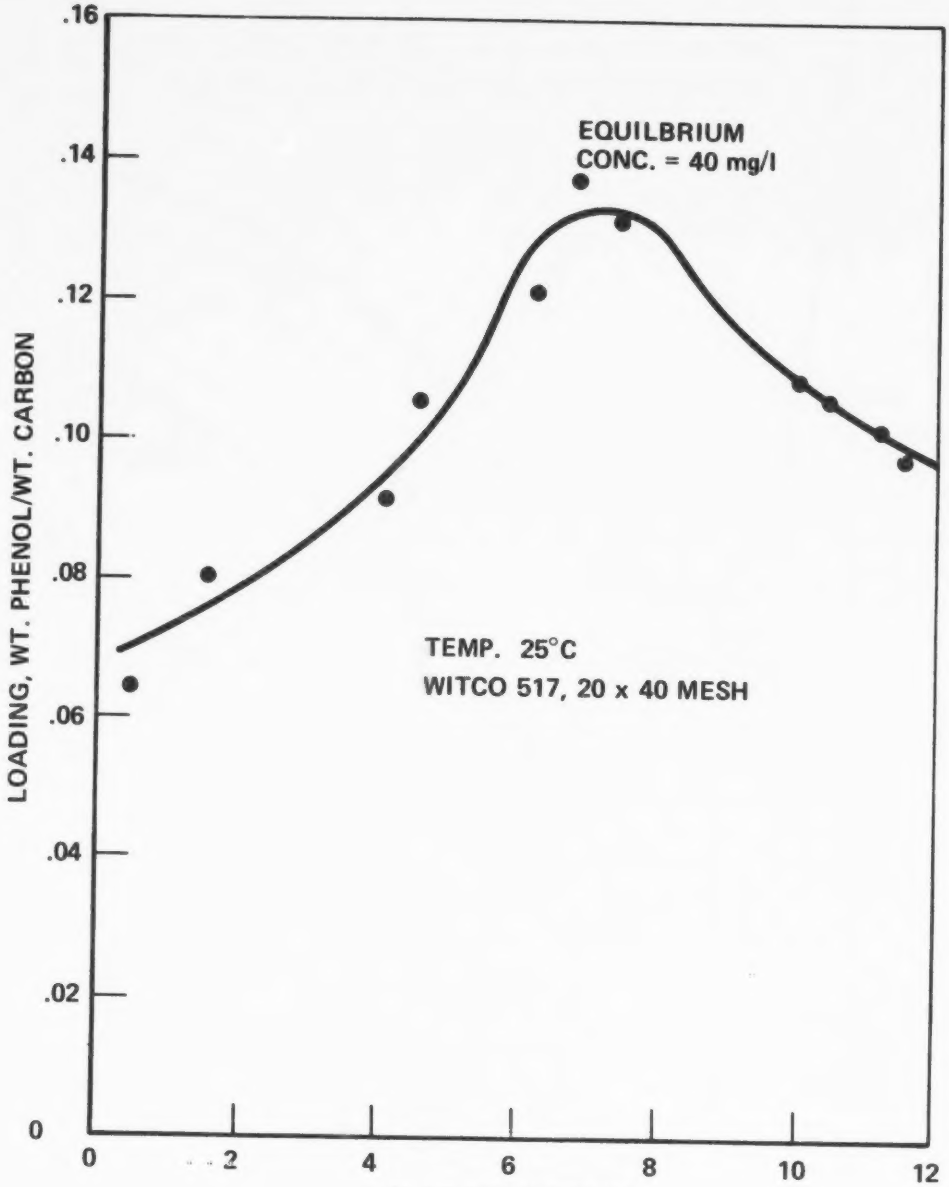


Figure 23
EQUILIBRIUM LOADING OF PHENOL ON CARBON vs pH

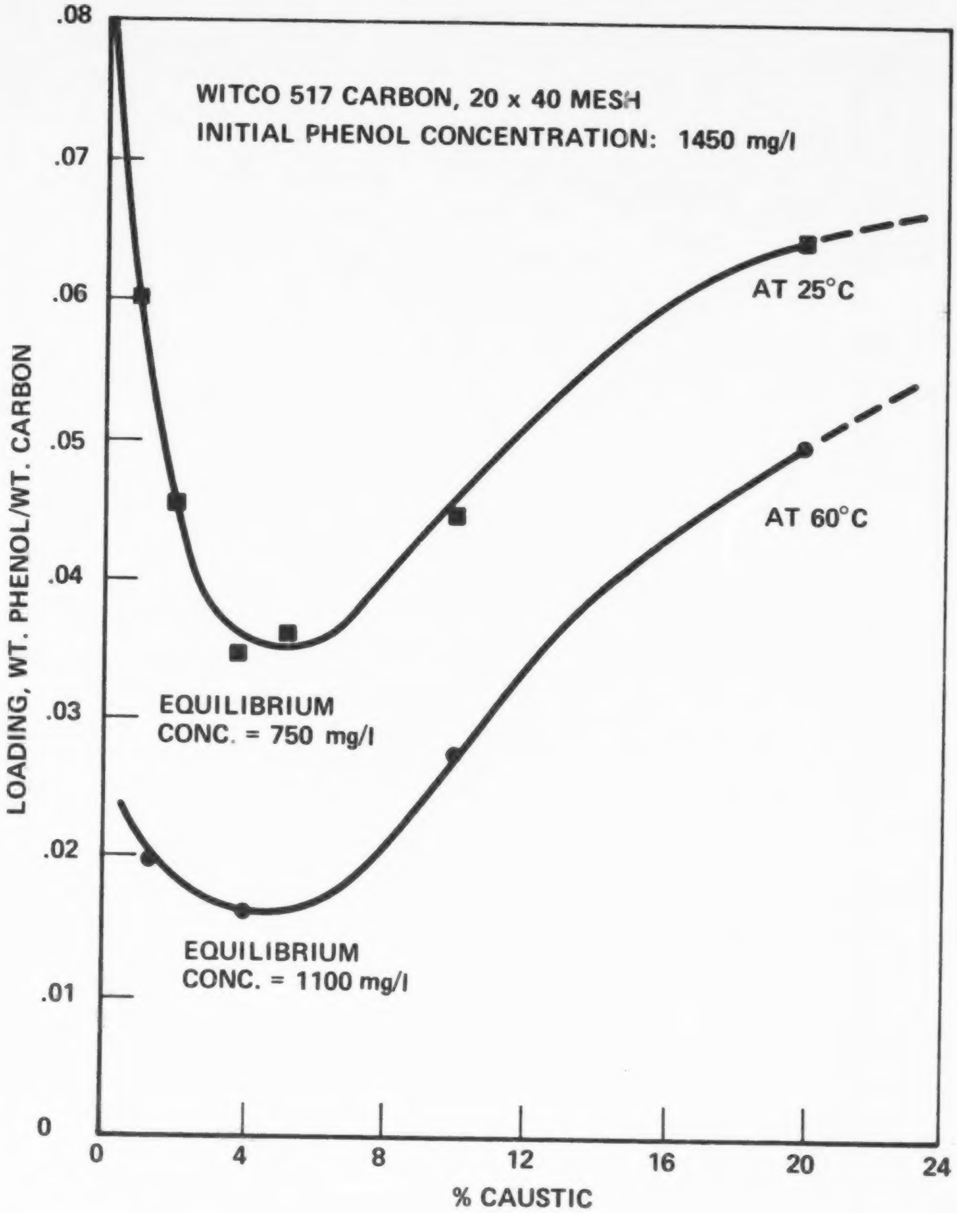


Figure 24

EQUILIBRIUM LOADING OF PHENOL ON CARBON vs % CAUSTIC

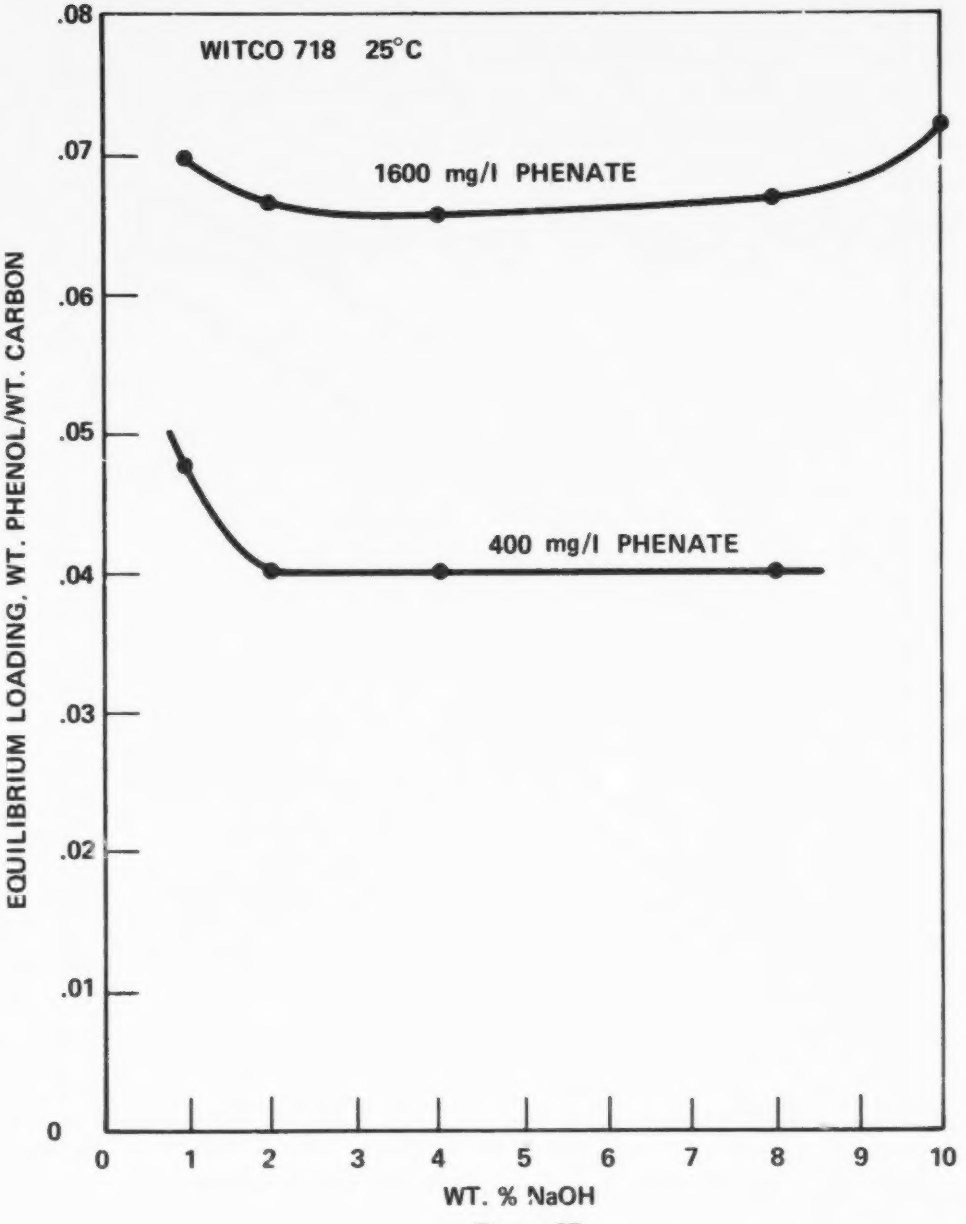


Figure 25

EQUILIBRIUM LOADING OF PHENOL ON CARBON vs % CAUSTIC AT TWO PHENATE CONCENTRATIONS

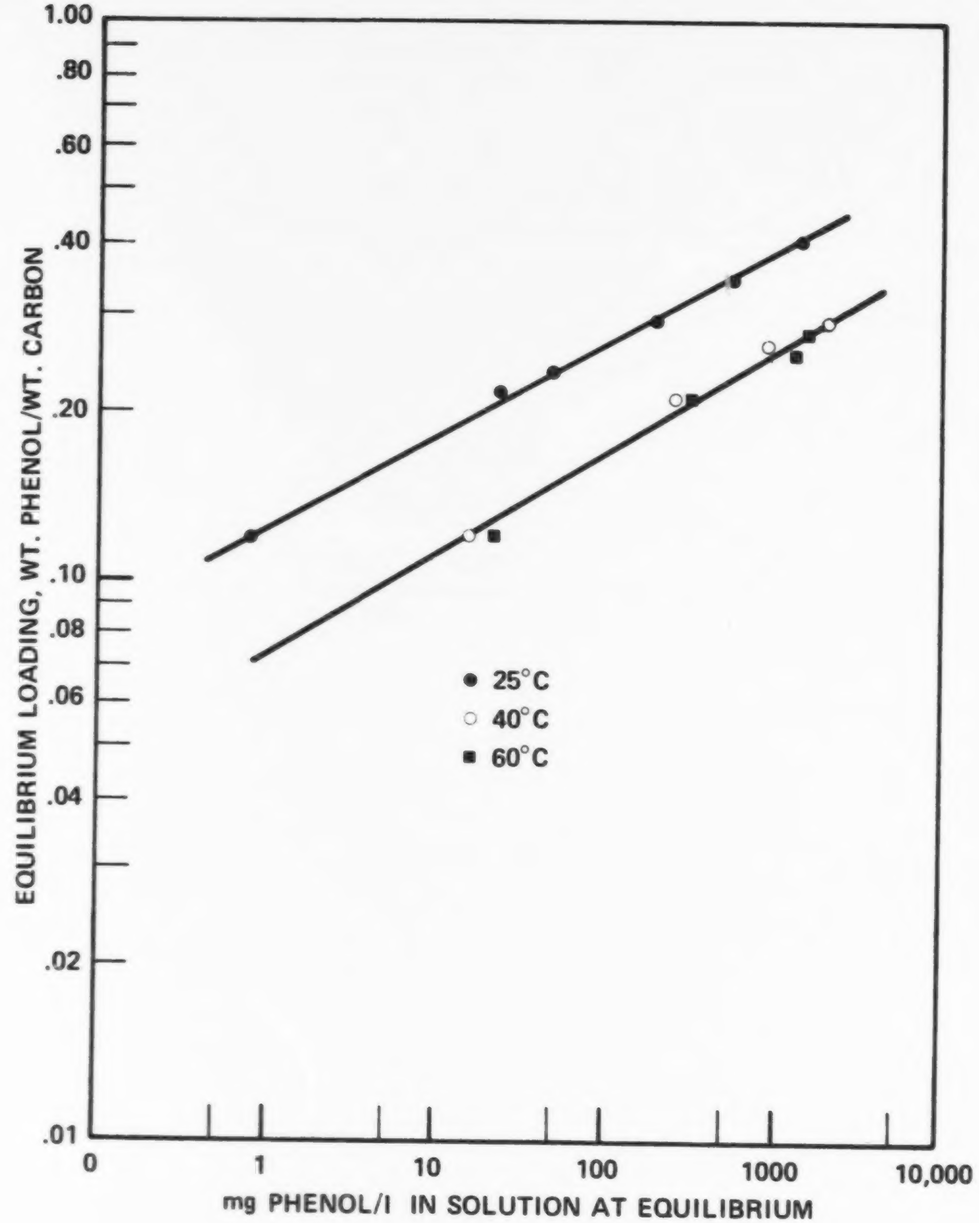


Figure 26

EQUILIBRIUM LOADING OF PHENOL ON ACID-WASHED WITCO 718 CARBON IN NEUTRAL 20% SODIUM CHLORIDE SOLUTION

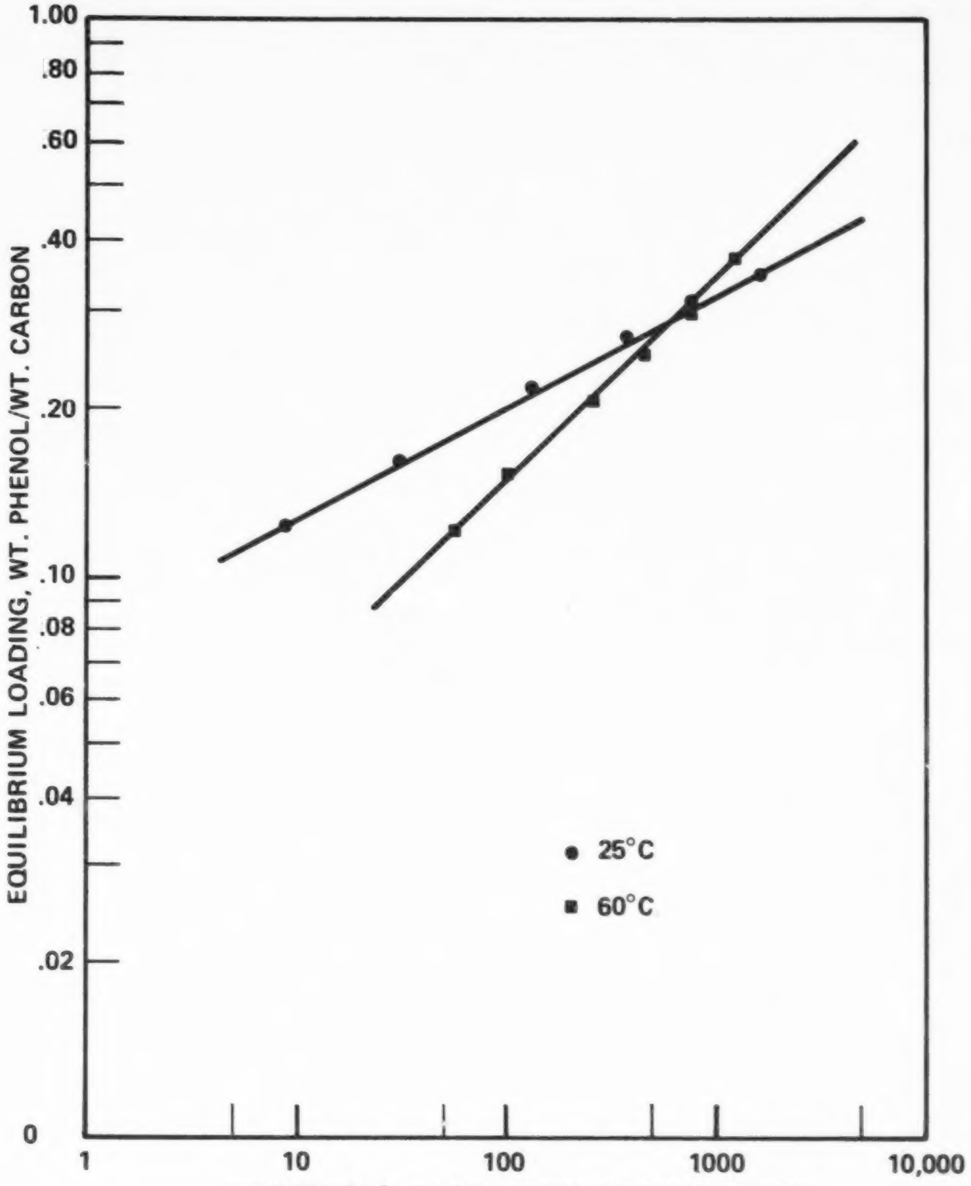


Figure 27

EQUILIBRIUM LOADING OF PHENOL ON ACID-WASHED NUCHAR WV-G CARBON IN NEUTRAL 20% SODIUM CHLORIDE SOLUTION

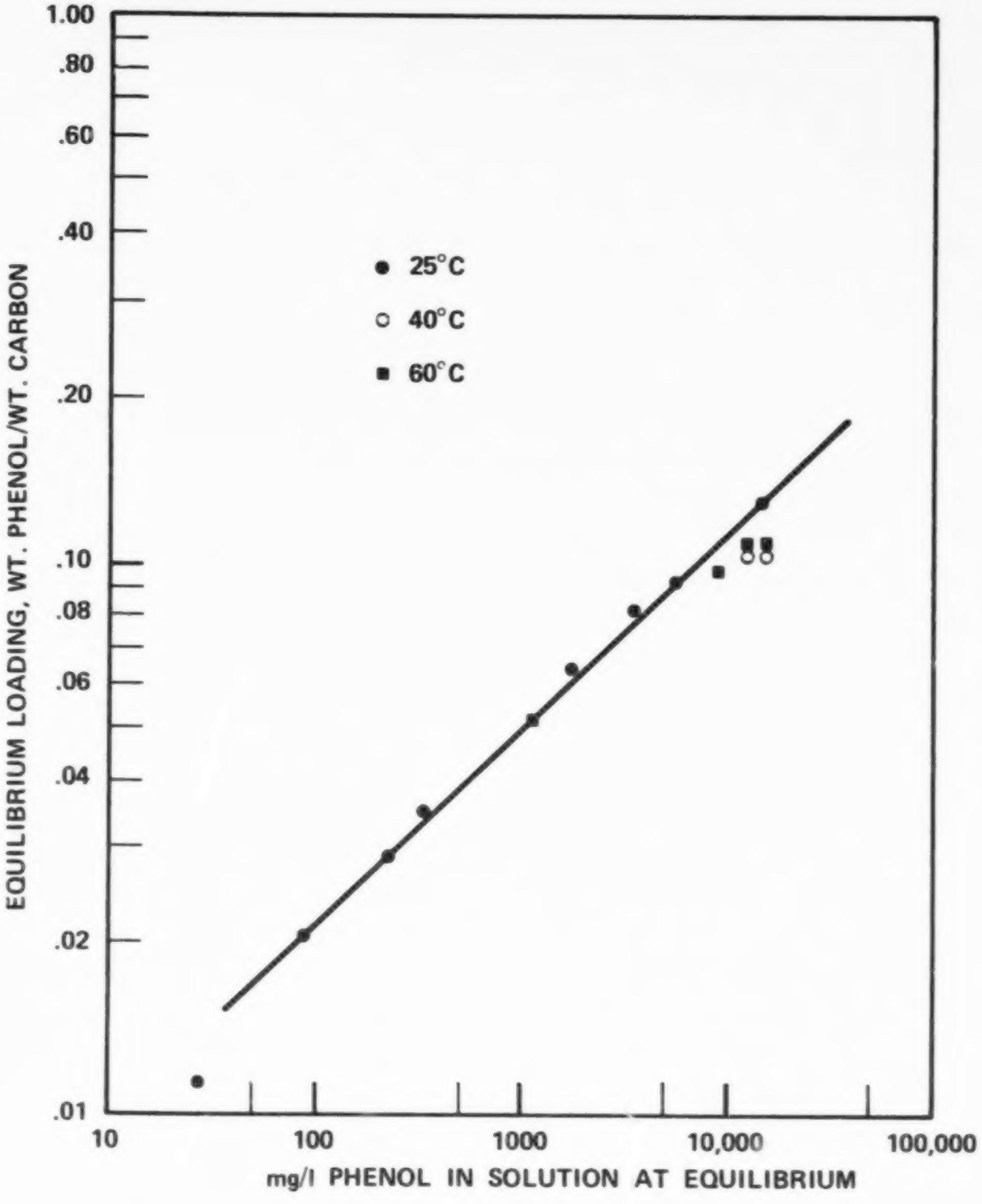


Figure 28

EQUILIBRIUM LOADING OF PHENOL ON ACID-WASHED WITCO 718 CARBON IN 2-4% CAUSTIC

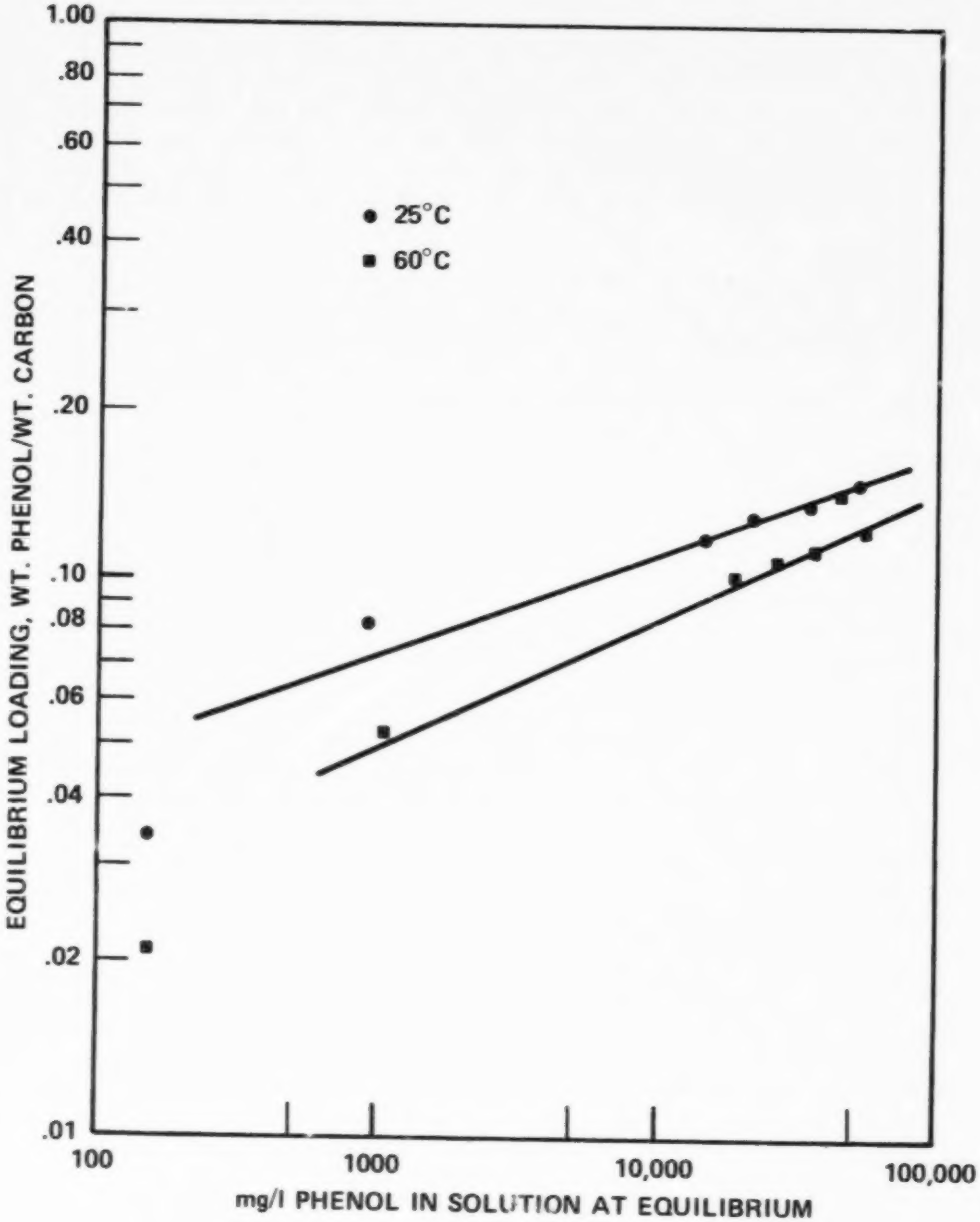


Figure 29

EQUILIBRIUM LOADING OF PHENOL ON ACID-WASHED NUCHAR WV-G CARBON IN 2-4% CAUSTIC has no effect for Witco 718. From these four curves, the loading that can be expected in column operations can be calculated if nearly equilibrium conditions are attained. The effective loading for each carbon is the difference between the adsorption and desorption loadings at the appropriate conditions. For example, if the phenol columns are regenerated at 60°C until the phenol concentration in the effluent is 500 mg/l, then the effective loadings for each carbon in near equilibrium with 200 mg/l feed at 60°C is calculated as 0.16 lb/lb for Witco 718 and 0.15 lb/lb for Nuchar WV-G. At 600 mg/l feed at 60°, the values are 0.2 for Witco 718 and 0.24 for Nuchar WV-G.

These batch equilibrium data on phenol adsorption and regeneration, were available for use in comparison with the actual performance of the Demonstration Plant.

Acetic Acid Adsorption and Regeneration

Similar to the program followed in laboratory studies of phenol adsorption, batch equilibrium studies on acetic acid adsorption were conducted to determine the best types of carbon to use in the Demonstration Plant and to examine further the acetic acid adsorption information which had been developed by earlier research and led to the selection of a two-stage carbon adsorption and caustic regeneration process for purification of this waste brine. The same sources and types of virgin carbon were initially screened for acetic acid capacity at 25°C with the results shown in Figure 30. Contrary to the results with phenol, significant differences to adsorb acetic acid were observed, with Witco 517, Nuchar WV-G, and Pittsburgh CAL showing the best results. Witco 517 was selected for further tests to check the effect of several variables. The kinetics of acetic acid adsorption and desorption were measured, and as expected with a small molecule such as acetic acid, they were rapid. Adsorption was essentially complete in 15 minutes for two different mesh sizes. Desorption was a little slower, requiring 30 minutes to reach equilibrium. The effect of pH on acetic acid loading was examined over the pH range 0 to 12, with the results shown in Figure 31. The optimum pH range is between 3 and 4. This curve also shows that acetic acid (as sodium acetate) loading on carbon at high pH values is very low, <0.003 lb/lb. Equilibrium loading studies with Witco 517 also indicated that salt had no effect on acetic acid loading, and that temperature had a marked effect. The equilibrium loading at 1500 mg/l acetic acid concentration was 0.067 at 25°C and 0.037 lb/lb at 65°C.

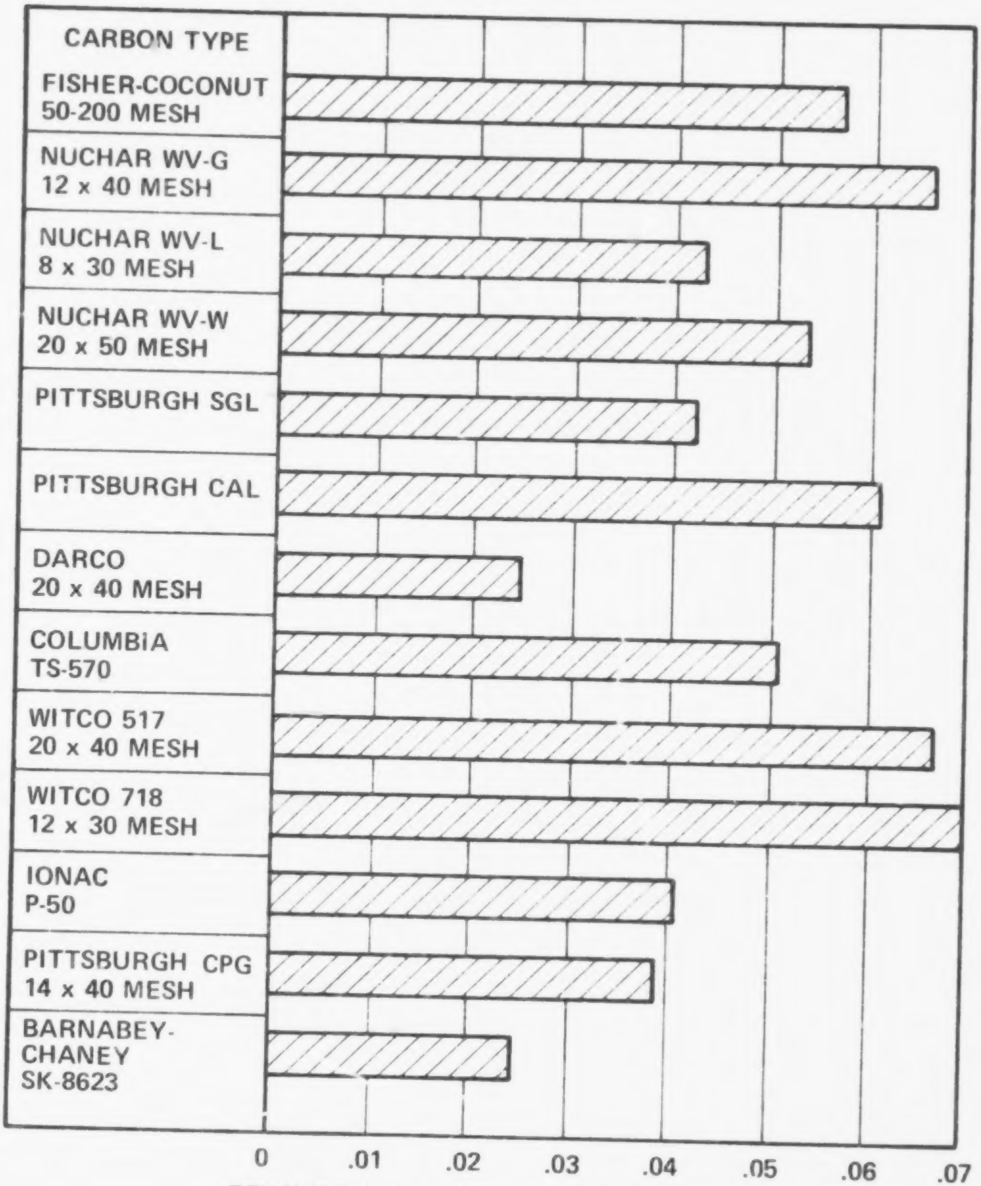


Figure 30

EQUILIBRIUM ACETIC ACID LOADING FOR VARIOUS VIRGIN ACTIVATED CARBONS

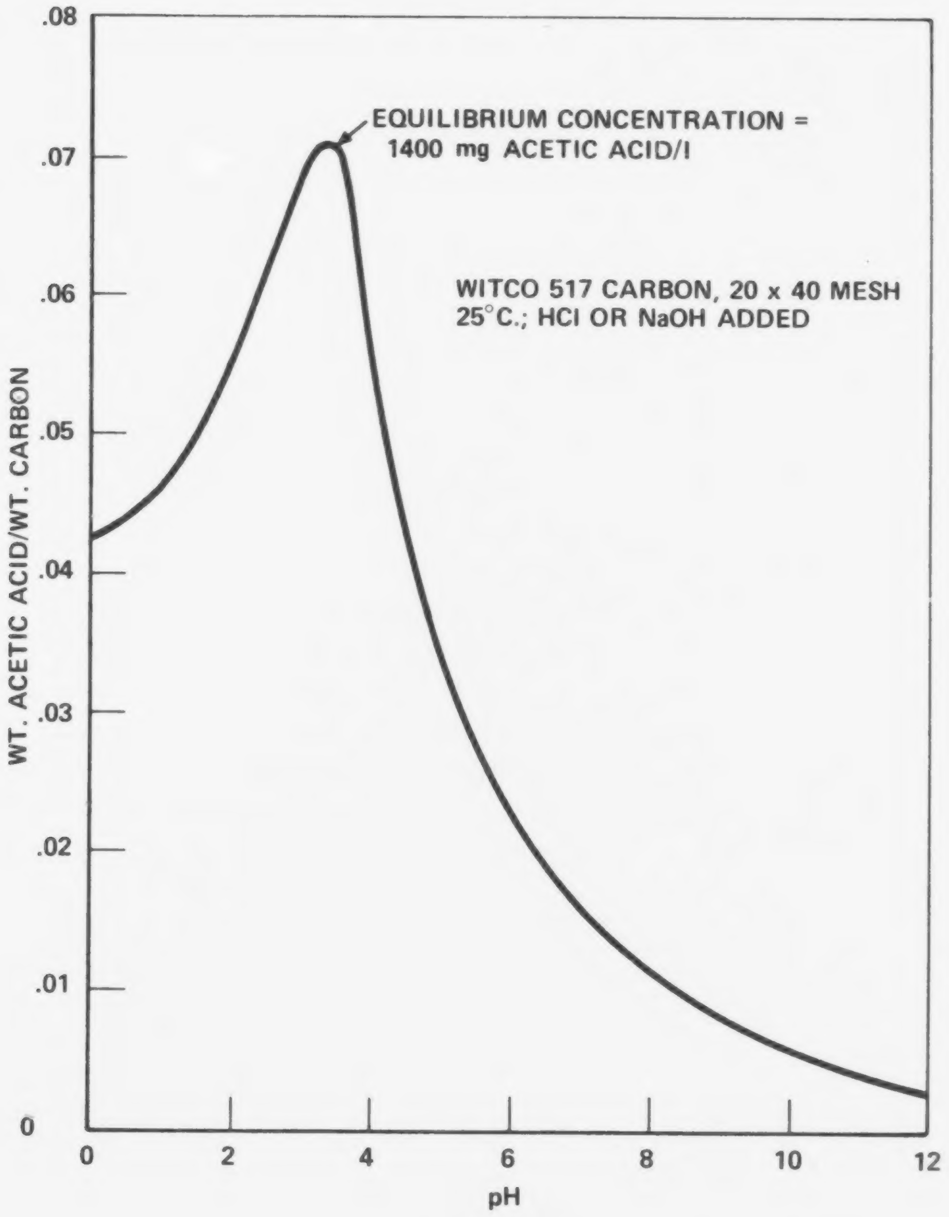


Figure 31
EQUILIBRIUM LOADING OF ACETIC ACID ON WITCO 517 CARBON vs pH

With the selection of Witco 718 and Nuchar WV-G carbons for the Demonstration Plant, adsorption isotherms were measured. At first, the carbons were run at 25°C and as received. The resultant isotherms are the top two curves in Figure 32. These data along with laboratory column evaluations formed the basis for comparison of the actual performance of these carbons in the Demonstration Plant. Recently, isotherms at 25°C and 60°C were measured on Witco 718 and Nuchar WV-G that had been acid-washed; they are also plotted on Figure 32. Surprisingly, these results indicate a marked decrease in the capacity of both carbons for acetic acid when they are acid-washed, and in all cases, Nuchar WV-G showed up better than Witco 718. These equilibrium data on the acid-washed carbons are not in agreement with the results obtained in the Demonstration Plant at lower temperatures. The loadings obtained at 25°-40°C were 0.04 to 0.06, much higher than the isotherm would predict.

Early in the grant period, acetic acid adsorption on Witco 517 and desorption with caustic was studied in a 1" I.D. x 8' high fixed bed. When treating a brine containing a high quantity of acetone (~350 ppm) the performance of the carbon with repeated adsorption-regeneration cycles slowly deteriorated. Loading decreased and the concentration of acetic acid in the effluent increased. This was postulated to be the result of the adsorption of acetone on the carbon and its subsequent conversion by a condensation reaction under caustic regeneration conditions to diacetone alcohol and larger molecules, resulting in gradual filling of the carbon pores with molecules not desorbable with caustic. This problem with acetone in the feed led to the setting of tight feed brine specifications on acetone content.

A composite sample was made of each of the truckload shipments of the actual carbons loaded into the Demonstration Plant columns. Part of this composite was evaluated in 1" I.D. x 8' high columns in the laboratory. The conditions used in this evaluation were a brine feed containing 1500 mg/l acetic acid at a flow rate of 2.0 gal/min/sq ft at pH 2 to 4. The results are presented in Table 8. In both evaluations, the carbon was not acid-washed prior to use. With Witco 718, this presented no problems. When this step was omitted for the Nuchar WV-G, the effluent brine from the first 3 cycles was of poor quality due to high pH. By the 4th cycle, performance was as expected. The data in Table 8 clearly show that the effective loading at a given temperature soon reaches a fairly constant value. Witco 718 exhibits a higher capacity than Nuchar WV-G. The effect of temper-

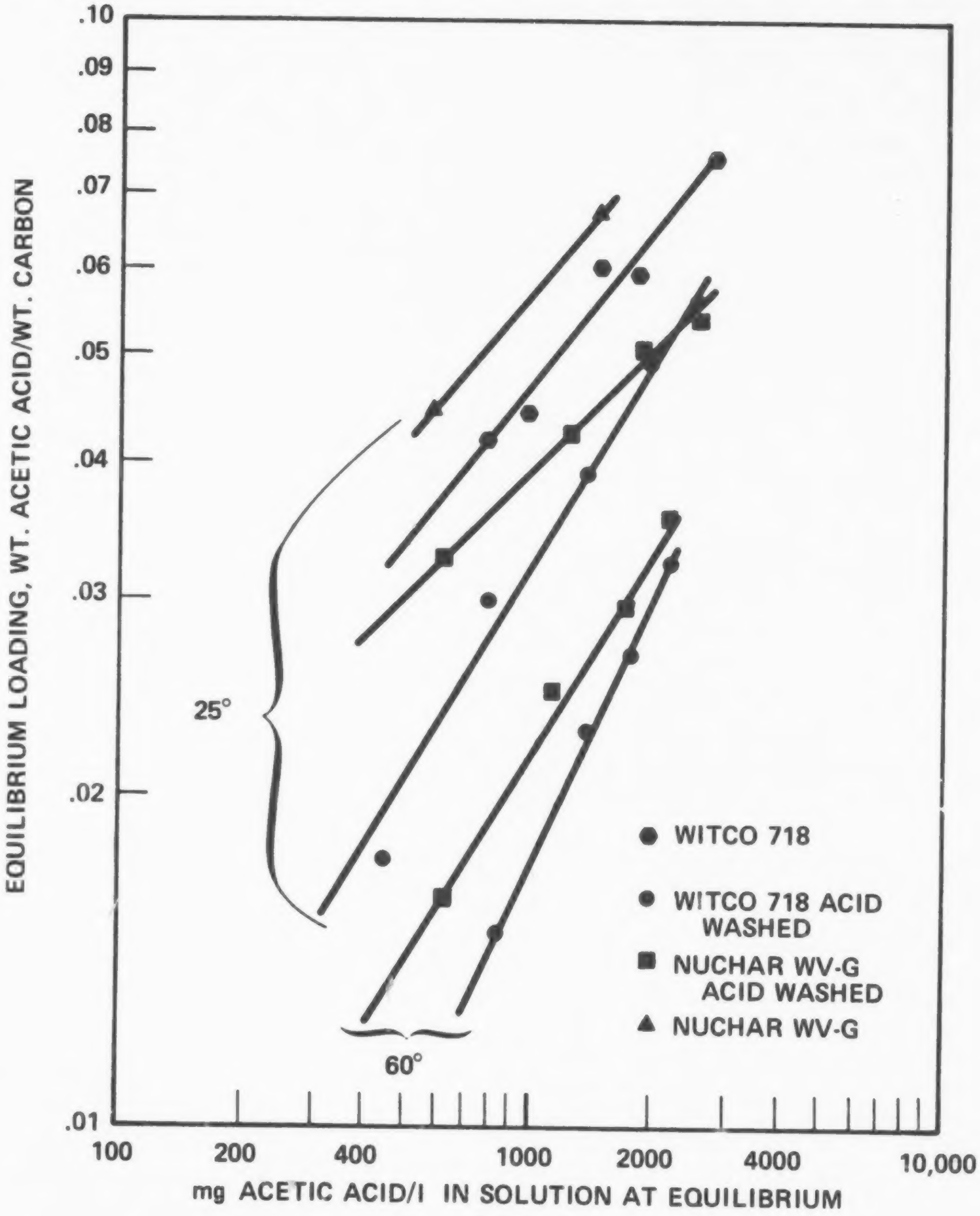


Figure 32

EQUILIBRIUM LOADING OF ACETIC ACID ON WITCO 718 AND NUCHAR WV-G CARBONS

TABLE 8

LABORATORY COLUMN EVALUATIONS OF DEMONSTRATION PLANT CARBON COMPOSITES

Column size: 1" x 8'
Flow : 2 gal/min/sq ft

WITCO 718, 12 x 30 Mesh, Composite

Cycle No.	Temp.	Acetic Acid Loading, lb/lb	Effluent Quality ppm NaOAc	ppm TOC
1	25	0.072	51	28
2	25	0.063	65	41
3	25	0.058	67	41
4	25	0.055	150	64
5	25	0.046	321	120
6	25	0.054	108	55
7	70	0.036	281	100
8	70	0.033	125	55

NUCHAR WV-G, 12 x 40 Mesh, Composite

Cycle No.	Temp.	Acetic Acid Loading, lb/lb	Effluent Quality ppm NaOAc	ppm TOC
1	25	0.025	327	120
2	25	0.034	282	100
3	25	0.032	483	180
4	25	0.044	30	25
5	25	0.042	42	30
6	25	0.043	12	21
7	70	0.021	45	33
8	70	0.017	92	54
9	25	0.034	142	68
10	50	0.029	74	45

ature on loading is also apparent. However, temperature has no real significant effect on the quality of the effluent, the results at 50° and 70°C being nearly equivalent to those at 25°C. This observation over a relatively few laboratory cycles does not correlate with the results obtained in the Demonstration Plant at high temperature and a great many cycles.

In all of the cycles run in this laboratory column evaluation of composites, the regeneration procedure was the same: 250-300 ml of 10% caustic, 100 ml of water, and 45 ml of 5N HCl were added sequentially. This 0.44 liters of total regeneration recipe represented one-third of an empty bed volume. The quantity and strength of these various reagents had been varied in several earlier 8' column runs to optimize the concentration of sodium acetate in the regenerant. In general, it was not affected. Peak sodium acetate concentrations of ~7% were achieved. The long, slow desorption experienced with phenol does not occur with acetic acid regeneration. After the peak concentration is reached, the acetic acid desorption curve has a good downward slope to low levels. In the laboratory columns, the volume of regenerant was 1.00 to 1.40 liters, or 7 to 10% of the volume of brine treated.

Physical Properties of Carbons

Mechanical Properties

The mechanical hardness or abrasion resistance of carbon is not as important in our fixed bed in-place regeneration application as it is in a process involving thermal regeneration. There the saturated carbon must be mechanically removed from the bed, transported to the furnace, passed through the furnace, and returned to a packed bed. In the course of obtaining isotherm data, a qualitative measure of abrasion resistance can be made when the granular carbon is tested as received. Since equilibrium is attained in a few hours with acetic acid and overnight with phenol, we did not feel that it was necessary to pulverize the granular carbon to obtain isotherm data.

In the course of obtaining isotherm data with granular carbon, we noted that some carbons gave clear supernatant liquid as soon as removed from the shaking apparatus, while other contained suspended carbon particles after standing for an hour. These suspended particles caused a general background absorbance when analyses were done spectrophotometrically, which changed little with wave length. Presumably a test could be developed by standardizing the variables such as time and vigor of shaking, time of settling, path length and wave length. In general, lignite base carbon gives the most fines, petroleum coke base carbons the least, with bituminous base carbons intermediate. The manufacturers' representatives are quick to indicate that fines produced from their carbons are a small fraction of the total carbon and merely represent the rounding of sharp projections on some granules. However, Witco carbon, for example, has nearly spherical granules as shipped and very few fines are generated by mechanical action in water suspension.

Composite samples of the Witco 718 and Nuchar WV-G used in the Demonstration Plant were tested for particle size distribution and comparative strength. The latter tests were conducted in the following manner. The carbon (200 g) was placed on a US No. 35 sieve. A US No. 40 sieve and pan were placed below the No. 35 sieve. A rotap shaker, built by W. S. Tyler Company, was used to impart mechanical energy to the tester. After 5 minutes of agitation, the tester was stopped and the amount of material on the No. 40 sieve and on the pan was determined. Agitation was again applied for an additional 55 minutes. After weighing the sieve and pan, 408 g of stones were added to promote breakage. The test was continued another 15 minutes. The results shown below indicate that there are differences between products with the Witco 718 composite being the better product both in particle size distribution and strength.

Sieve Analyses, Composite Samples

US Sieve Number	Weight Percent on Sieve: Nuchar	Weight Percent on Sieve: Witco
8	nil	nil
10	0.03	nil
12	0.69	1.81
14	9.98	22.15
16	23.84	34.59
18	27.39	25.15
20	19.14	10.72
30	16.05	4.82
50	2.63	0.56
100	0.03	0.06
-100	0.22	0.14

Breakage Tests

Product Test Time	Weight % On Nuchar -35 + 40	Nuchar -40	Witco -35 + 40	Witco -40
5 min	2.17	0.56	0.34	0.24
60 min	2.27	1.22	0.35	0.31
add 406 gm stones				
15 min	5.35	8.97	1.22	4.60

Surface Properties

Composite samples were also tested for physical properties normally measured on solid catalysts. The results are given below:

	Surface Area m^2/gm	True Density g/cc	Total Porosity %
Witco 718	1176	2.42	66.9
Nuchar WV-G	1226	2.16	63.3

It is interesting that the carbon with slightly higher surface area has less total porosity. The apparent density, as measured with mercury at 1.8 psia, was the same, 0.89 g/cc, for both carbons. Thus, the Witco particle probably has denser walls.

Activated carbons are usually characterized by reference to their capacity to adsorb a particular molecule under specified conditions. Some reference molecules include phenol, carbon tetrachloride, chloropicrin, methylene blue and iodine. There is sentiment among workers in the field of advanced waste treatment that iodine number may correlate with desirable carbon utility in their area. However, A.S.T.M is still working on standardizing the conditions for this one reference molecule.

Thus, it is obvious that it would be highly desirable if some physical property could be measured for all commercially available carbons which would enable one to at least select a small group of carbons for evaluation each time adsorption is indicated for treatment of a new industrial byproduct stream. Such a physical property might be pore size distribution. One could scale data on available carbons and select those possessing a large percentage of their pore volume in the size range appropriate to the molecule of interest.

Mercury Porosimetry is a standard way to obtain information on pore size distribution. The 5000 psi penetrometer is believed to provide data to 350 Å pore diameter[1]. In the case of small molecules like acetic acid and even phenol, very little adsorption would occur in pores this large. These are probably the passageways to smaller pores. Specifically, only 22% of the pore volume of Witco 718 and 34% of the volume of Nuchar WV-G is available to mercury at 5000 psi.

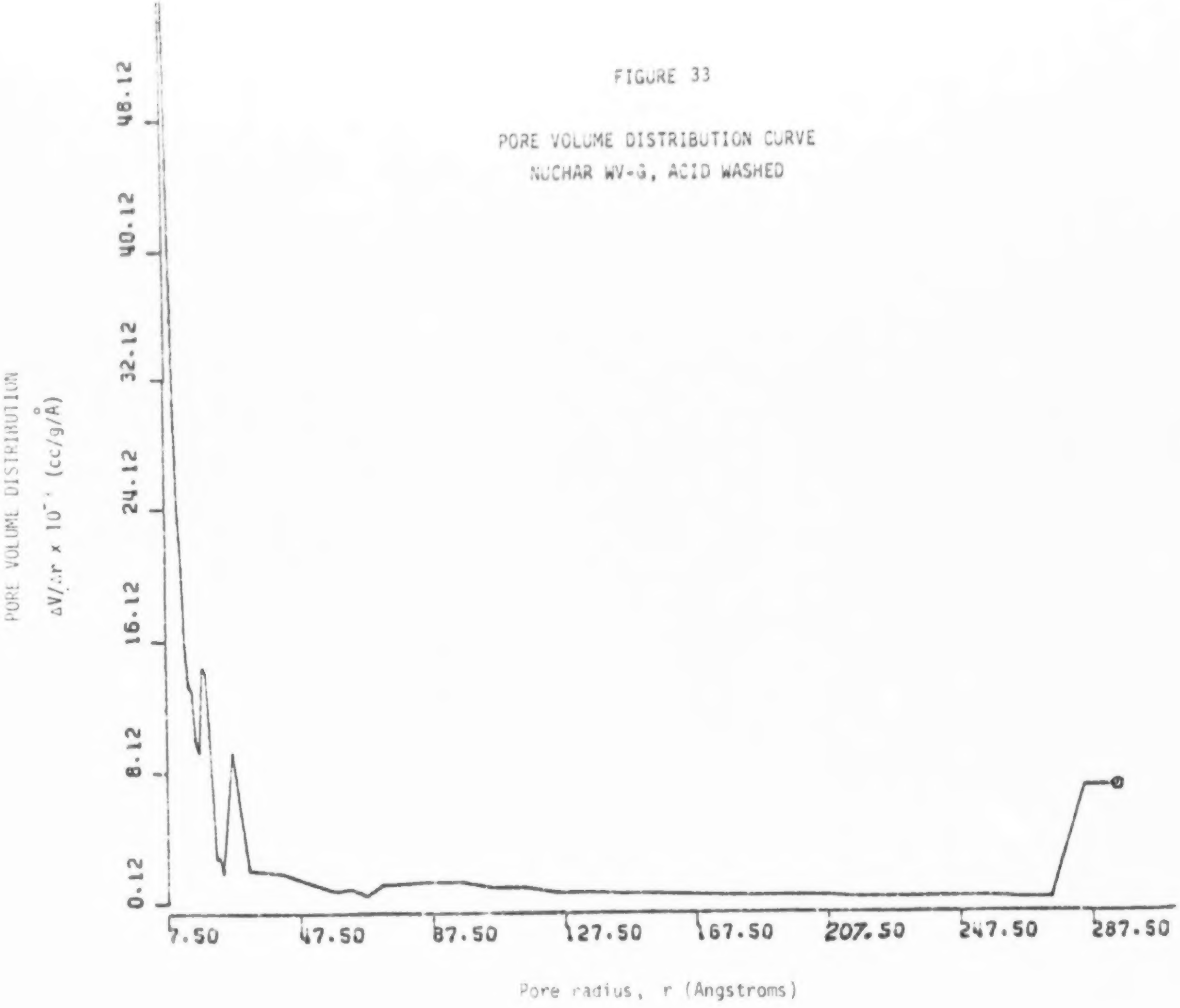
A mercury porosimeter usable to 60,000 psi was also available. This is believed to correlate with pore diameters down to 30 Å[1], which is still probably large for acetic acid and phenol. The data showed a reasonably smooth increase in penetration with pressure for both carbons, with Nuchar having more penetration than Witco in the range of 500 to 60,000 psi. Witco was beginning to gain on Nuchar above 30,000 psi. Acid-washing the carbon increased the penetration at all pressures in the above range, with the effect being more pronounced for Nuchar. Since Nuchar has more inorganic ash, this result with acid-washing is plausible.

By determining the "complete" nitrogen desorption isotherm, information on pore diameters down to about 15 Angstroms can be obtained[2]. This is a much slower procedure than the standard B.E.T. surface area measurement, requiring about a week per sample, providing no experimental mishaps such as leakage occur during the long experiment. From the desorption curve, a pore volume distribution curve can be derived. This information can also be presented in the form of a cumulative pore volume curve.

Four samples were submitted; Witco 718 and Nuchar WV-G, both as received and acid-washed. The pore volume distribution curves are given in Figures 33 through 36, showing the increase in pore volume with increasing pore diameter. Acid-washing eliminates some pores in the 50 to 100 Angstrom radius range with both carbons. This may be responsible for the drop in capacity for acetic acid or phenol observed when both carbons are acid-washed. With both acid-washed carbons, the bulk of the pore volume is at very small radius. It is not understood what causes the negative pore volume indicated with Witco carbon at about 10 Å radius. In conclusion, no

FIGURE 33

PORE VOLUME DISTRIBUTION CURVE
NUCHAR WV-G, ACID WASHED



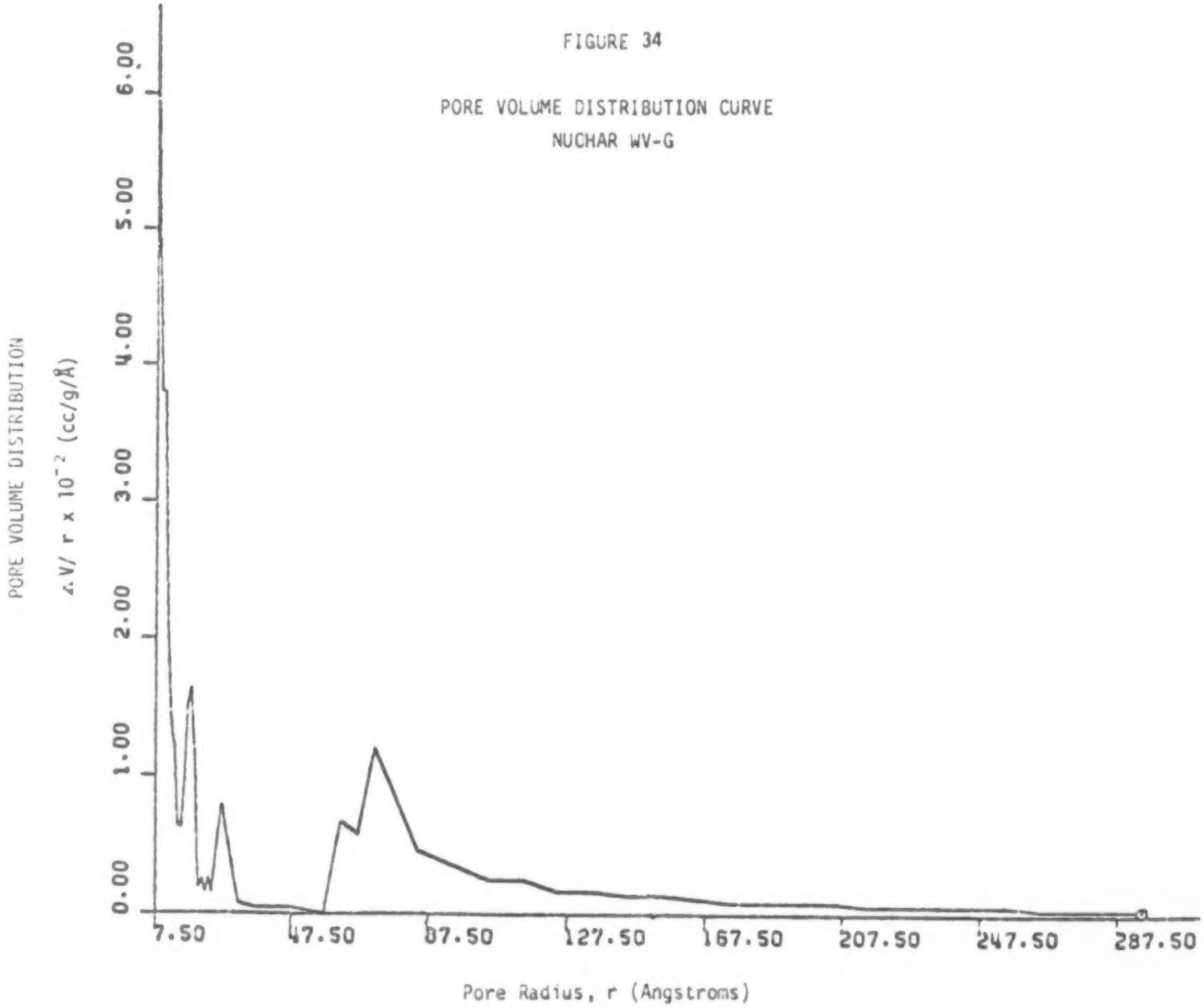


FIGURE 34

PORE VOLUME DISTRIBUTION CURVE
NUCHAR WV-G

FIGURE 35

PORE VOLUME DISTRIBUTION CURVE
WITCO 718, ACID WASHED

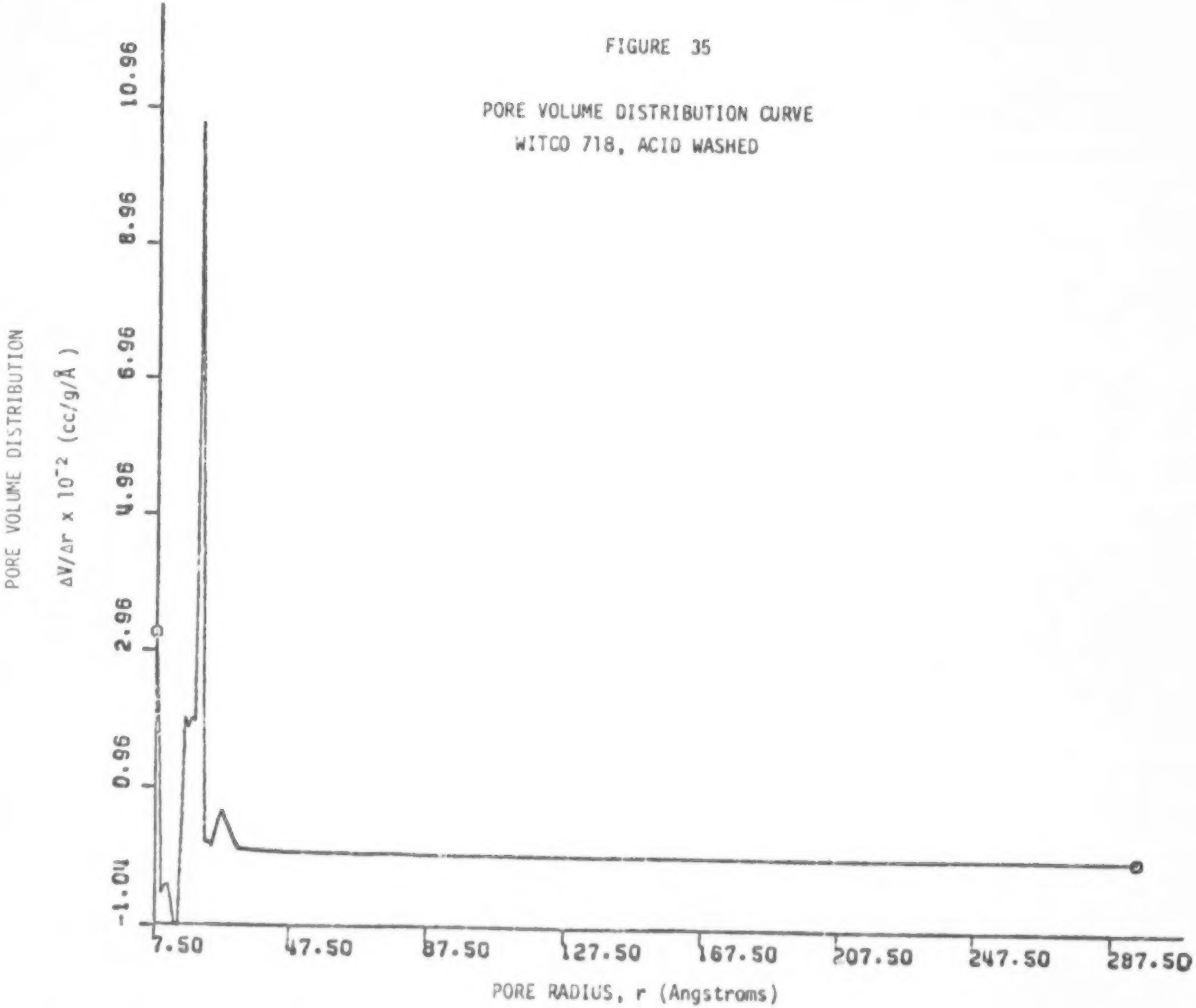
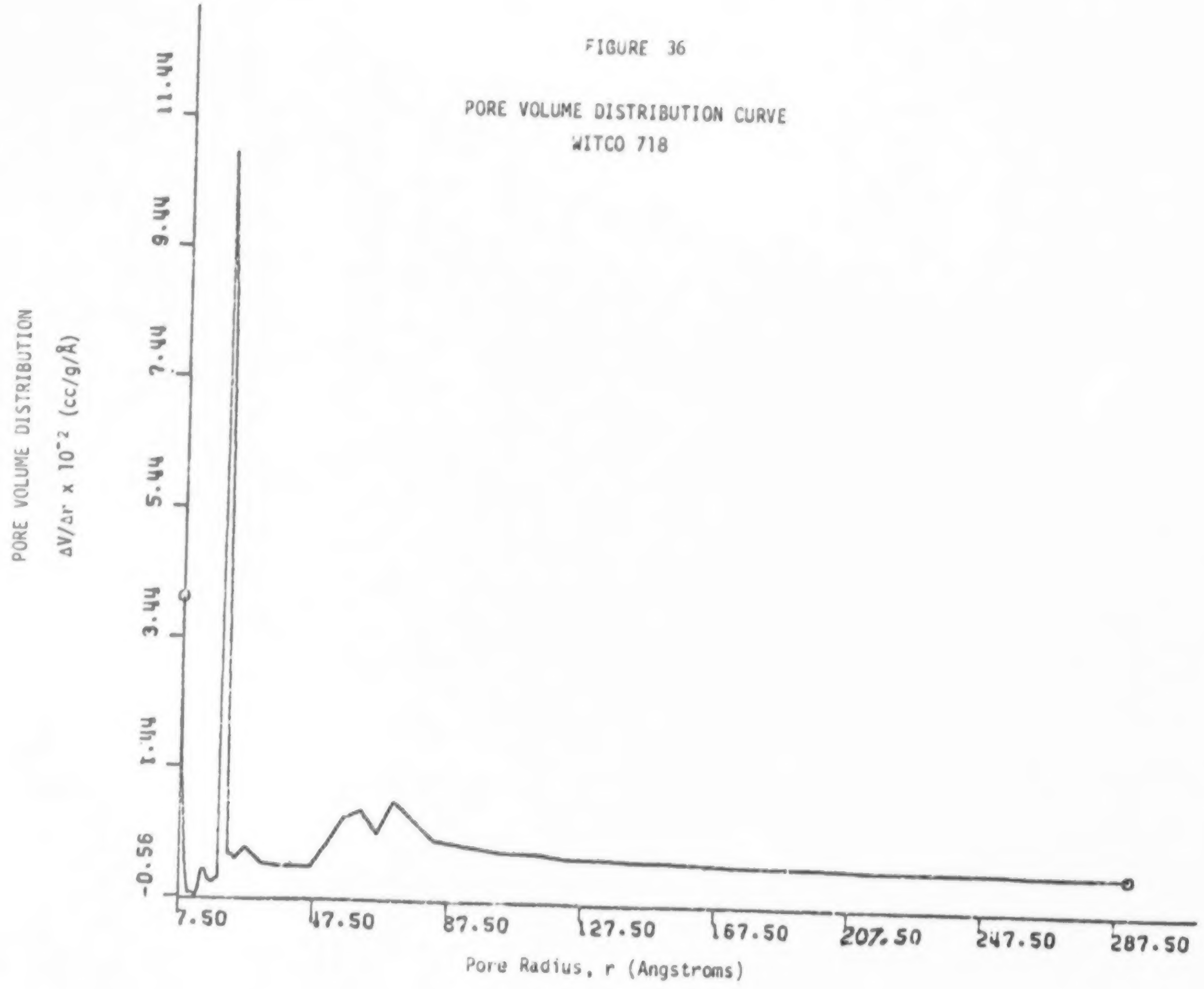


FIGURE 36

PORE VOLUME DISTRIBUTION CURVE
WITCO 718



satisfactory correlation between physical properties and performance was obtained. The "complete" nitrogen isotherm seems the most likely source of useful information at this time. Similar data on a variety of carbons should be obtained and compared with data obtained on reference compounds.

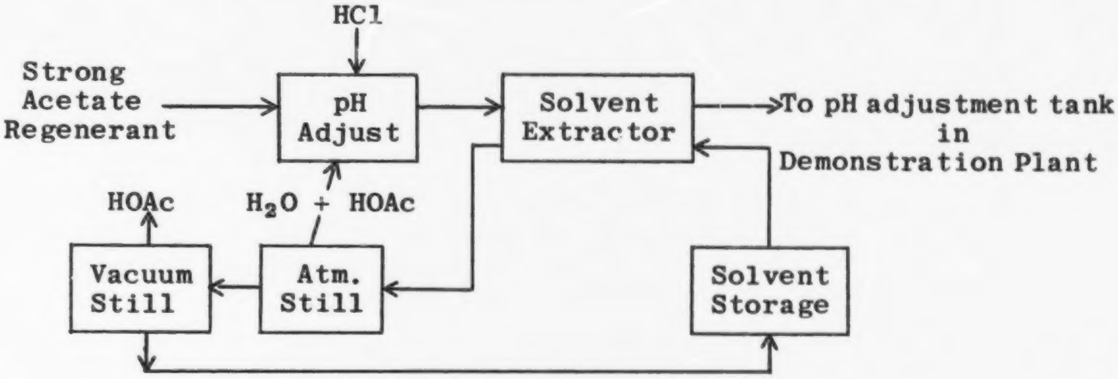
Acetic Acid Recovery

To complete the picture on byproduct recovery from the waste brine, laboratory studies were conducted on the recovery of a useful byproduct from the sodium acetate regenerant. There is very little internal plant consumption of sodium acetate or acetic acid esters that might be synthesized from the regenerant. If an anhydrous acetic acid could be derived from the regenerant, there would be an internal use.

For any recovery process, it would be advantageous to build up the acetate concentration as high as possible in the regenerant. Modifications were made in the Demonstration Plant to save the last half of regenerant, add fresh caustic, and reuse this as the first regenerant on the next column. This was accomplished in a single tank where two would have been desirable. However, the volume of regenerant was reduced 30-40%. The acetate concentration in the strong regenerant was increased to 40-60 g/l as acetic acid by these changes. The first approach considered to producing acetic acid was to boil off as much of the water as possible, then add as strong HCl as possible, preferably anhydrous HCl. The mixture of water and acid could be distilled and dried by a well known azeotropic system[3]. Since large amounts of NaCl are formed when the regenerant is acidified, and the salt precipitates out during the boil down of the acid brine, special equipment would be required to handle the salt separation. Since the azeotropic drying system necessarily involves some kind of organic solvent to act as a water entrainer, solvent extraction is a reasonable alternate and was the second approach considered.

One of the standard solvents used in azeotropic drying of acetic acid is ethylene dichloride. It is not a good extraction solvent for acetic acid from water. Butyl acetate is a better extractant and a good water entrainer, but since it can be present in only limited amounts in the drying system, it can not be used in the quantity required to do a good solvent extraction. The two best extractants found in our earlier work were t-butyl alcohol and tributyl phosphate. The only azeotropic data available on a butanol-acetic acid system are for the normal isomer which boils too close to acetic acid. Since propanol is reported as non-azeotropic with acetic acid, it is possible that the lower boiling butyl alcohols are also non-azeotropic with acetic acid. However, any solvent which boils lower than acetic acid has the disadvantage that all of the solvent would have to be vaporized leaving acetic acid as a bottom product.

A high boiling solvent, such as tributyl phosphate had the advantage that acetic acid can be stripped as an overhead product without expenditure of energy for vaporization of the solvent. A simplified block diagram of such a process is given below.



Strong acetate regenerant is acidified to pH 3 with HCl, then contacted with the solvent to remove ~90% of the acetic acid. The raffinate phase, a strong brine containing acetic acid, is pumped to the pH adjustment tank where it is combined with the regular brine flow and put through the acetic acid adsorber. The extract phase is distilled to remove water, then acetic acid. The water overhead, rich in acetic acid, is recycled to the strong acetate tank. Tributyl phosphate (TBP) the solvent of choice, is not stable in the presence of acetic acid above about 200°C. Thus, a vacuum still would be required to strip acetic acid from the solvent.

Since regeneration is a batch operation, the recovery system could also be a batch process rather than continuous. In this case, one tank could serve as the strong acetate wash storage tank and the pH adjustment tank and batch extractor. Also, a single still could serve both distillation functions indicated on the block diagram. This scheme would reduce the capital requirements at the expense of operating costs.

The brine effluent from the solvent extractor will be saturated with TBP; in brine its solubility is only ~50 ppm, whereas, in water, it is ~6000 ppm. At 50 ppm, 1.3 lb/day of solvent is lost. This is too little to justify a stripper to remove the TBP. If fed back into the Demonstration Plant at the pH adjustment tank, TBP would adsorb on the top of the acetate beds. Here it would be hydrolyzed at the extremes of pH it would experience. This proposed acetic acid recovery process has two unique features compared to the practice in wood distillation or pulp mill black liquor recovery. A solvent is used which is insoluble enough in brine to eliminate the necessity for stripping the raffinate. The other feature is that the solvent is high boiling so that acetic acid can be distilled from the solvent rather than the usual practice of distilling the solvent, always the larger quantity, away from the residual acetic acid. The reason for a volatile solvent in the two industries mentioned is doubtless the necessity to avoid solvent loss in the tars they must contend with. Our regenerant contains no tar.

Assuming optimum regeneration efficiency, the scale of this acetic acid recovery system, at 100 gpm in the Demonstration Plant, could be as low as 4 gpm in the brine circuit and 2 gpm or less in the solvent cycle.

At an acetic acid concentration in the brine of 1500 mg/l and 6¢/lb credit for acetic acid, there is $100 worth of acetic acid per day to be recovered. After paying operating costs, there would not be enough value to support the capital cost of a recovery unit. With the acetic acid level in the incoming brine having recently decreased to ~1000 ppm, acetic acid recovery is even less favorable.

SECTION IX

MATHEMATICAL SIMULATION OF ACTIVATED CARBON ADSORPTION SYSTEMS

The design of adsorption equipment and the prediction of its performance for a range of operating conditions have been based on prior experience and large amounts of experimental data. The unsteady-state and nonlinear nature of adsorption systems made the evaluation of scale-up factors and performance prediction difficult. In this section, a mathematical model is described that allows reliable prediction of the performance of large scale systems on the basis of data from relatively simple and inexpensive laboratory experiments and from related experiments and correlations reported in the literature. The ability to predict performance is a major step in the progression of the design of adsorption equipment and the specification of operating conditions from an art to a science.

The mathematical model is merely a mathematical description of the various inter-relationships that exist among the process variables. In the development of the model approximations are made to simplify the model and to speed up its numerical solution. The approximations are judiciously selected such that simplicity and computing speed are not attained at the expense of model accuracy. The first approximation is the familiar lumped parameter approximation[4]. That is, the adsorption column is divided into axial sections, and the properties (temperature, concentration, etc.) of each volume section are lumped into average values for the section. In essence, the adsorption column is considered to be a series of ideal stirred tank reactors. The lumped parameter approximation transforms the mathematical model from a system of partial differential equations to a system of ordinary differential equations. An additional benefit of the lumped parameter approximation is that the same model can be used to predict the performance of both batch adsorbers and column adsorbers. A batch adsorber is simply a column with one axial section.

The mass balance for the jth axial section reduces to:

$$\frac{dc_j}{dt} + \frac{\rho_b}{\epsilon}\frac{d}{dt}w_j = \frac{F}{V_j\epsilon}(C_{j-1} - C_j) \qquad (1)$$

$$j = 1, \ldots, NAS$$

where j = axial section number, number consecutively in direction of flow

C_j = concentration of adsorbate in solution in jth axial section (mass/volume)

t = time

ρ_b = bulk density of adsorbent (mass/volume)

ϵ = bed void fraction (volume/volume)

w_j = weight of adsorbate per weight of adsorbent in jth axial section (mass/mass)

F = flow rate (volume/time)

V_j = volume of jth axial section (volume)

NAS = number of axial sections

The next step is to specify how the loading (weight of adsorbate per weight of adsorbent) changes with time, dw_j/dt. This is accomplished by specifying the controlling mechanism and then expressing that mechanism in terms of the process variables. Three resistances can be identified for the adsorption of adsorbate onto an adsorbent - transport across an external "stagnant" film, diffusion within the adsorbent, and surface reactions[5].

It is assumed that the surface reactions are relatively rapid, and that the rate of adsorption is controlled by resistance to mass transfer.

Transport of adsorbate from the bulk liquid across the "stagnant" film to the external surface of the adsorbent is related to process variables by means of a mass transfer coefficient[6].

$$\frac{dw_j}{dt} = \frac{ka}{\rho_b \rho_l} (C_j - C_j^*) \qquad (2)$$

where k = liquid phase mass transfer coefficient (moles/area/time/mole fract.)

a = interfacial area per unit volume (area/volume)

ρ_l = solution molal density (moles/volume)

C_j^* = concentration of adsorbate in solution adjacent to external surface of adsorbent (equilibrium is assumed at the solution-adsorbent interface) (mass/volume)

Transport of adsorbate within the adsorbent occurs by both diffusion in the fluid occupying the intra-particle voids and diffusion along the walls of the internal voids. A homogeneous solid diffusion mechanism is assumed to account for the transport of adsorbate within the adsorbent[7].

In this model, the solid is taken to be homogeneous with no distinction made between the solid itself and the intra-particle voids. Application of the mass balance to the homogeneous solid diffusion model results in the familiar second-order parabolic partial differential equation for diffusion in homogeneous medium[8].

Again, the lumped parameter approximation is used to reduce the partial differential equation to a system of ordinary differential equations. The adsorbent particles are assumed to be spherical and of uniform size. The lumped parameter approximation divides the adsorbent particles into equal volume spherical shells and assumes uniform conditions within each shell. The mass balances for adsorbate on the adsorbent reduce to

$$\frac{d}{dt} q_{j,r} = \alpha_r (q_{j,r+1} - q_{j,r}) - \beta_r (q_{j,r} - q_{j,r-1}) \tag{3}$$

$$j = 1, \ldots, NAS$$
$$r = 1, \ldots, NRS$$

where r = spherical shell number, number consecutively from center of particle out

$q_{j,r}$ = weight of adsorbate per weight of adsorbent in rth radial shell in jth axial section (mass/mass)

$q_{j,o} = o$

$q_{j,NRS+1}$ = adsorbate loading in equilibrium with solution at solution-adsorbent interface

$\alpha_r = \dfrac{D_s A_r}{DR_r \, DV_r}$

$\beta_r = \dfrac{D_s A_{r-1}}{DR_{r-1} \, DV_r}$

D_s = homogeneous diffusivity (area/time)

A_r = area of outer surface of rth spherical shell (area)

DR_r = average of the thickness of the rth and r+1th spherical shells (length)

DV_r = volume of rth spherical shell (volume)

NRS = number of spherical shells

The total adsorbent loading is related to the spherical shell loadings as follows

$$w_j = \frac{1}{NRS} \sum_{r=1}^{NRS} q_{j,r} \tag{4}$$

$j = 1, \ldots, NAS$

An additional relationship is required to complete the specification of the rate of change of loading and that is the equilibrium relationship that exists at the solution-adsorbent interface

$$q_{j,NRS+1} = E(C_j{}^*) \tag{5}$$

$j = 1, \ldots, NAS$

where E is the adsorption equilibrium relationship

To complete the model, it is necessary to specify initial conditions and boundary conditions. The appropriate initial conditions are

$$\left.\begin{array}{l} C_j(t=0) = C_j^\circ \\ C_j{}^*(t=0) = C_j^* \\ w_j(t=0) = w_j{}^\circ \\ q_{j,r}(t=0) = q_{j,r}^\circ \end{array}\right\} \begin{array}{l} j = 1, \ldots, NAS \\ \\ r = 1, \ldots, NRS \end{array} \tag{6}$$

and the boundary conditions are

$$C_\circ(t) = C_f(t) \tag{7}$$

where C_f is the concentration of adsorbate in the feed.

The mathematical model thus consists of equations 1 to 7. The numerical solution of this model is accomplished by starting with the initial conditions and predicting conditions within the column and in the effluent by marching forward in time. By linearizing the equilibrium relationship an extremely efficient computing algorithm can be developed.

The following quantities are required as input data for the model:

1) dimensions of carbon bed
2) physical properties of carbon - particle size
   bulk density
   bed void fraction
3) physical properties of solution - density
4) equilibrium between solute in solution and on the carbon
5) transport parameters - mass transfer coefficient
   solute diffusivity in carbon
   The mass transfer coefficient comes from a literature correlation while the diffusivity is determined from batch kinetic experiments
6) initial conditions in carbon bed
7) feed conditions as a function of time

Three applications of the model to the phenol/Witco 718 system are illustrated in Figures 37, 38, and 39 respectively: correlation of batch kinetic data, prediction of a regeneration curve, and prediction of a breakthrough curve.

Batch kinetic experiments (both adsorption and desorption) were run to determine parameter values for diffusion within the carbon particles. The data from one kinetic experiment are illustrated in Figure 37 and compared with the predictions of the model. In this experiment, 0.5 g of phenol-free Witco 718 carbon was initially shaken with 10 ml of water to drive air out of the internal voids. Then, 90 ml of 1000 mg phenol/l solution was added. The points on Figure 37 are the experimentally measured phenol levels at 25°C as a function of the time elapsed after the addition of the phenol solution to the carbon. The curve on Figure 37 is the change in phenol level that is predicted by the model. The correlation is excellent, indicating that the program is a good model of the actual physical adsorption process.

On Figure 38, the measured phenol levels in the Witco 718 phenol adsorber effluent during the fourth regeneration are indicated by the points. The curve on Figure 38 is the effluent phenol level that is predicted by the model. Again, the agreement between the actual data and the model is good. The peak phenol concentration is predicted and the shape of the curve is close to actual.

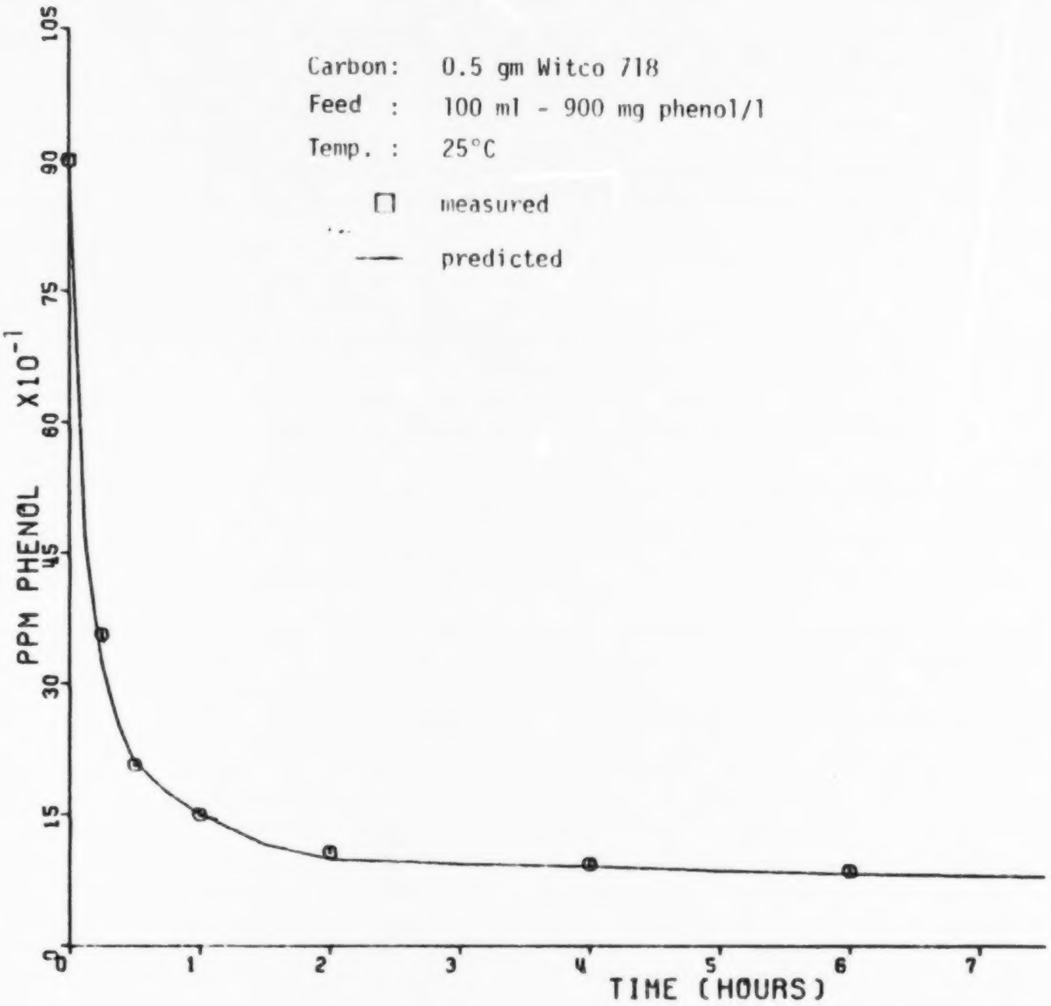


FIGURE 37

BATCH ADSORPTION OF PHENOL ON WITCO 718 CARBON
PREDICTED BY MATHEMATICAL MODEL COMPARED
TO EXPERIMENTAL DATA

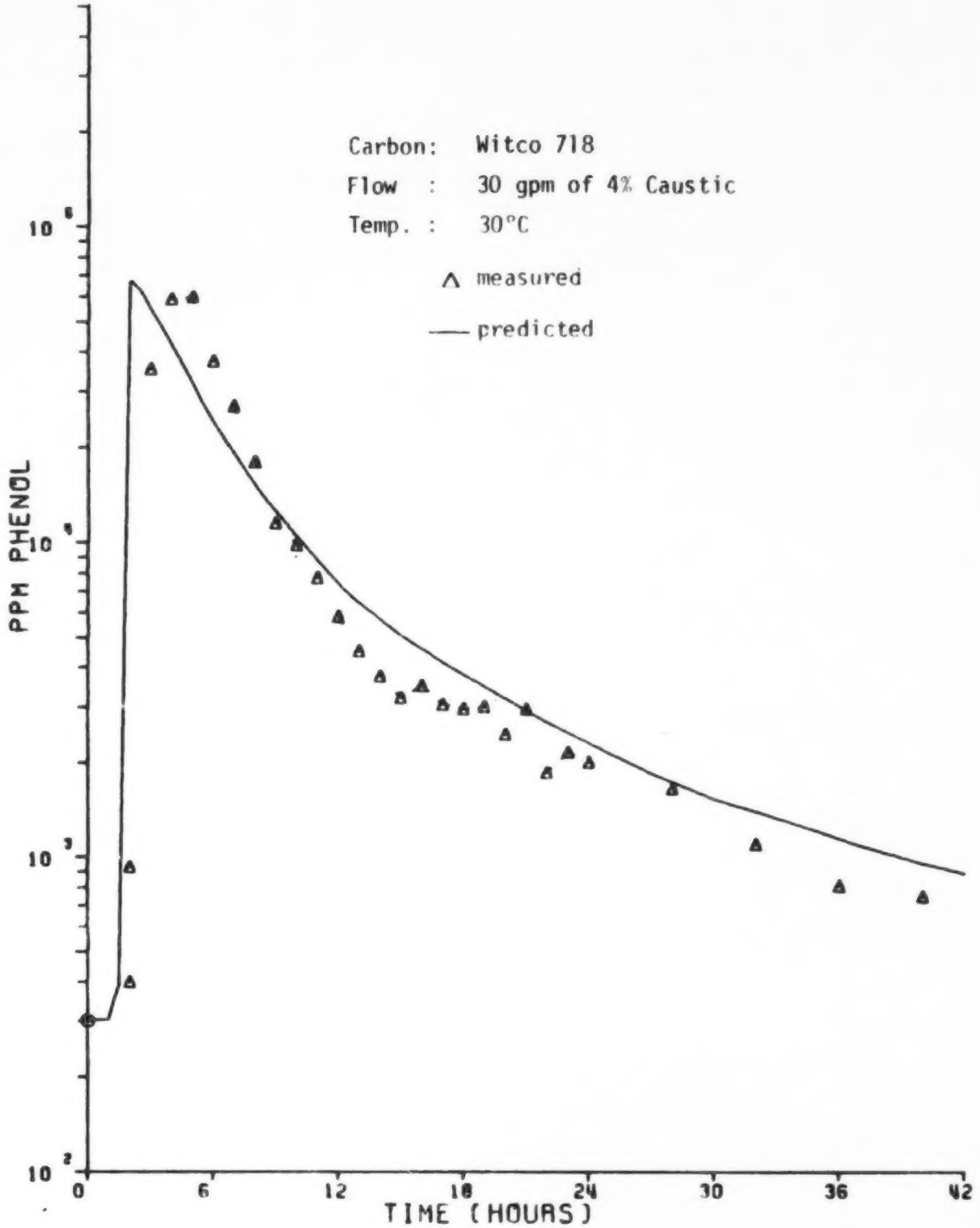


FIGURE 38

PHENOL DESORPTION FROM WITCO 718 CARBON
PREDICTED BY MATHEMATICAL MODEL COMPARED TO
ACTUAL DATA FROM PHENOL ADSORBER REGENERATION NO. 4

On Figure 39, a predicted breakthrough curve for the Witco 718 phenol adsorber is illustrated. For this curve, the feed conditions are 100 gpm, 250 ppm phenol, and 25°C. No actual breakthrough curve under these conditions is available for comparison.

On the basis of data from only small laboratory experiments and literature correlations, the model does a very good job of predicting the performance of large columns. The model is a valuable tool for use in the design of adsorption systems and in the evaluation of operating conditions.

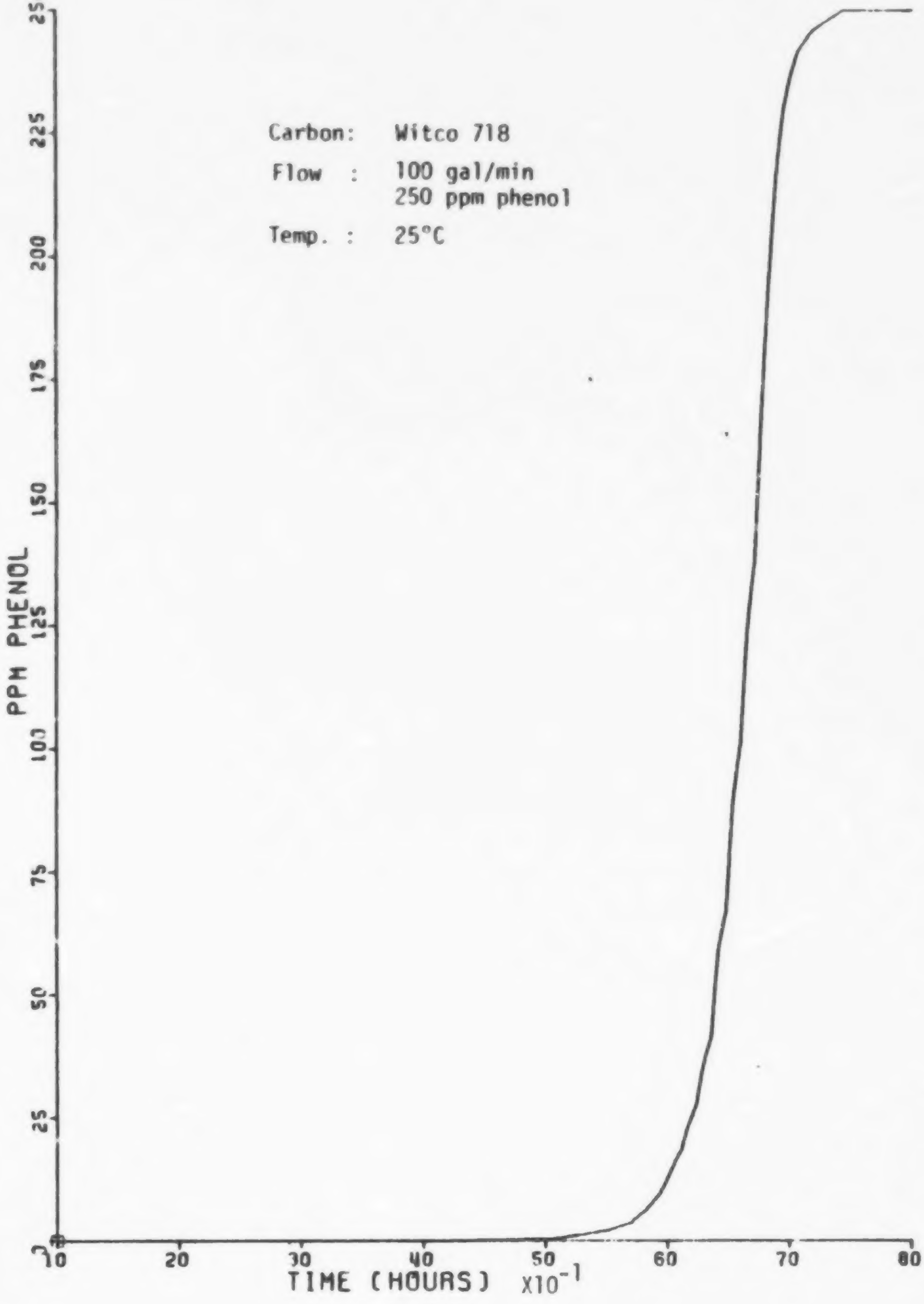


FIGURE 39

BREAKTHROUGH CURVE PREDICTED BY MATHEMATICAL MODEL FOR DEMONSTRATION PLANT PHENOL ADSORBER

SECTION X

ACKNOWLEDGEMENTS

This project was performed by the Environmental Research Laboratory at the Midland, Michigan Division of the Dow Chemical, U.S.A. Dow personnel participating in the project were Dr. R. A. Gaska, Project Manager, Mr. R. D. Fox, Project Supervisor, Mr. C. J. Pinamont, Superintendent of the Demonstration Plant, Dr. R. T. Keller, Senior Research Chemist in charge of laboratory studies, Mr. C. K. Bon, in charge of the chlorine test cell evaluation, and Dr. G. G. Hoyer, who developed the mathematical model.

Design engineering for the Demonstration Plant was performed by Dow Process and Plant Engineering, with Mr. W. L. Bennett serving as Project Engineer, and Mr. Lyle Martz as Process Engineer. The site and foundation contractor was Collinson Construction Corp of Midland, Michigan. The general and mechanical contractor was Kaighin, Hughes, and Paulin of Toledo, Ohio.

We wish to acknowledge the helpful cooperation, assistance, and guidance provided by the Project Officer, Mr. Clifford Risley, Jr., of the Office of Research and Monitoring, Region V, U.S. Environmental Protection Agency, Chicago, Illinois.

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SECTION XI

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SECTION XII

PUBLICATIONS

1. "Purification of a Waste Brine by Carbon Adsorption with Emphasis on Wastewater Reuse", R. D. Fox, R. T. Keller, C. J. Pinamont, and J. L. Severson, presented at the 25th Purdue Industrial Waste Conference, May 6, 1970.

2. "Brine Purification and Byproduct Recovery by Activated Carbon Adsorption", R. D. Fox, R. T. Keller, C. J. Pinamont, presented at the 64th Annual Meeting, American Institute of Chemical Engineers, November 30, 1971.

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SECTION XIII

GLOSSARY OF ABBREVIATIONS

M - one thousand
HOAc - acetic acid
NaOAc - sodium acetate
DMK - acetone
ØOH - phenol
Bz - benzene
≤ - less than or equal to
mu - millimicrons
µl - microliter
TOC - Total Organic Carbon

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SECTION XIV

APPENDIX

Analytical Procedures

Analysis for Acetic Acid

At concentrations greater than about 500 ppm, titration with a base was satisfactory since no significant amount of other weak acids were present in our sample. The Demonstration Plant operators performed the titrations. Below about 500 ppm, the samples were sent to the Analytical Laboratory for nuclear magnetic resonance analysis using a computer average transient for greater sensitivity and tetrolic acid as an internal standard.

A Sargent-Welch recording titrator, Model DG was used in the pH mode at 10 pH units span and automatic rate. A 10 ml burret was used which gives 5 inches of chart per ml. Sodium hydroxide N/10 was the titrant. The pH was adjusted to about 2 with hydrochloric acid solution in a dropping bottle, 1N for neutral or slightly acid samples and 5N for regenerant samples. The sample size varied from 20 ml to 0.5 ml depending on the amount of acetic acid present with the object of having 1 to 3 feet of chart paper between inflections. The titrator was adjusted to shut itself off at pH 10 so that no operator attention was required after the titration was started. The inflections between strong and weak acid and between weak acid and strong base were determined visually, and the inches of chart paper between inflections was counted on the chart paper. The concentration of acetic acid was then calculated as follows:

$$\text{g HOAc/l} = \frac{\text{inches between inflections}}{\text{ml of sample}} \times \frac{6}{5}$$

Analysis for Phenol

These analyses were done by the operators using a Beckman DBGT spectrophotometer. The samples were made strongly basic and the absorbance was measured at 307, 287, and 267 mu in a 1 mm cell. The net absorbance was calculated as follows:

$$A_{net} = A_{287} - A_{307} - 1/2\,(A_{267} - A_{307})$$

The mg phenol/l was then read from a plot of concentration vs net absorbance covering a range of zero to 300 mg phe-

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nol per liter. If the reading was off-scale, dilution was made to bring the net absorbance below 0.6. This method was unreliable below about 5 mg phenol/l. Such samples were sent to another laboratory where they were extracted with chloroform and the extract was then analyzed by ultraviolet spectrometry in up to 100 mm cells.

Analysis for Acetone and Benzene

These analyses were done by gas chromatography on 6' x 1/8" of Porapak® Q column support at 175° and 30 psi of helium carrier gas pressure. A three μl sample was injected and peak heights were compared with a standard of 10 μl/l benzene and 50 μl/l acetone in water. Under these conditions, the acetone peak appeared in 3 and the benzene in 6 minutes. Phenol also gave a peak in about 30 minutes but the recorder was usually on standby at this time, and the information was not used. The operators ran this analysis using an Aerograph 600D chromatograph.

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